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SUPERCRITICAL GAS EXTRACTION OF COAL : INVESTIGATION OF THE CHEMICAL AND PHYSICAL FACTORS

FINAL REPORT

BY

RAYLO CHEMICALS LIMITED

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SUBJECT:

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RAYLO CHEMICALS LIMITED BY
DR. J.F. PRESCOTT AND
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FINAL REPORT

SUMMARY

Supercritical gas (scg) extraction of Forestburg subbituminous coal with toluene modified by the addition of 1 to 25% of a co-solvent was carried out in order to define the properties of an effective extraction medium. The addition of free radical initiators did not result in enhanced coal pyrolysis but did contribute to the formation of bibenzyl, a toluene degradation product. Polar compounds generally did not enhance the coal pyrolysis reaction nor aid in the recovery of coal derived liquids (cdl). Tetrahydrofuran did, however, appear to have a positive effect on cdl recovery. Solvent modification with the hydrogen donating compound tetrahydronaphthalene (tetralin) resulted in a much greater degree of coal pyrolysis. The optimum amount of tetralin addition is about 8 to 10% on a weight basis. Two other possible hydrogen donating solvents, indane and decalin had little or no effect on the pyrolysis of coal or the isolation of cdl.

Studies extending the temperature range of supercritical toluene extraction of Forestburg subbituminous coal lead to the conclusion that the optimum extraction temperature is between 400 and 420°C. Temperatures beyond 450° resulted in thermal polymerization of toluene. Extending the pressure of the extraction to 4500 psig lead to the conclusion that the optimum pressure lies between 2300 and 3000 psig. Pressures in excess of 3000 psig did not significantly enhance the recovery of cdl.

Pooled cdl from supercritical toluene extraction of Forestburg coal at temperatures ranging from 350 to 450° and pressures ranging from 1100 to 1900 psig were analyzed using standard techniques. Solvent analysis showed that the cdl consists of about 50% pentane soluble material (oil or maltene), 25% asphaltene, 10% preasphaltene and about 10% tetrahydrofuran insoluble residue. The oil had an average molecular weight of 267 and a H/C ratio of 1.37 (0.78 for the starting coal). Liquid chromatography of the oil shows that polar compounds make up 32% of the total oil.

I. INTRODUCTION

The Department of Supply and Services awarded a contract (23SQ-23440-0-9111) to Raylo Chemicals Limited to investigate the physical and chemical factors affecting supercritical gas (scg) extraction of coal.

Raylo had used a semi-continuous extraction unit capable of attaining temperatures up to 450° and pressures up to 2000 psig to establish that scg extraction was a feasible means of liquefying coal. However, data at higher temperatures and pressures were needed before construction of a fully continuous unit could be justified. Raylo commissioned Pressure Products Industries to design and construct a reactor autoclave capable of attaining 600°C and 6000 psig.

Previous work had shown that the properties of the extracting solvent had a profound effect on the coal pyrolysis reaction and on the isolated yields of coal derived liquids (cdl). These effects could not be attributed solely to physical effects and chemical interaction between the solvent and the pyrolyzing coal was clearly indicated. A major effort was mounted to define the properties of an effective supercritical solvent.

The work in this final report was originally reported in Raylo Progress Reports I through XIII covering the period from March 1, 1981 to March 31, 1982. This report unifies the data generated during this period.

II. DESCRIPTION OF COAL SAMPLES

Previous studies were carried out using aliquots of a single 100 kilogram sample of Forestburg subbituminous coal obtained from Luscar Coal Company in December 1979 (Sample 1). This coal was crushed, comminuted and sieved. The 12-24 mesh material was used.

A new 100 kilogram sample of Forestburg subbituminous coal was obtained from Luscar Coal Company in May 1981 (Sample 2) for the current series of experiments. This material, supplied as ten inch lumps, was crushed and comminuted into a powdered material containing particles ranging in size from 1/8 inch to -24 mesh and was used in this form for the extraction experiments. Table I tabulates the proximate analysis and calorific value of both coal samples, Table II tabulates the ultimate analysis and Table III compares the results of scg extraction with toluene at 400° and 1500 psig.

The composition of sample 2 was closer than that of sample 1 to the typical composition of Forestburg subbituminous coal (Table I). Nevertheless, the results of supercritical toluene extraction were remarkably similar for the two samples. The extent of coal pyrolysis, indicated by char yield, was not affected by particle size. The use of unsieved coal appeared to result in a somewhat higher isolated yield of cd1.

III. SOLVENT MODIFICATION STUDIES

Previous work had shown that toluene was an effective solvent for scg extraction. Other pure solvents were also tested for their efficacy as scg solvents. The oxygenated solvents, isopropyl alcohol, methyl ethyl ketone and p-cresol (diluted to 90% with water) were all found to decompose during the extraction conditions (1). The paraffinic solvents, n-heptane and n-decane did not have enough solvent power to dissolve cdl to be considered as scg extraction solvents. A preliminary experiment using tetrahydronaphthalene (tetralin) dramatically affected both the extent of coal pyrolysis and the isolated yield of cdl.

None of the above solvents, toluene excepted, could be used as an scg extraction solvent. However, any of the above solvents could conceivably be used to advantage as an additive to modify toluene. A number of solvents were added to toluene at levels of one to 25 weight percent to determine the type of solvent that would favourably influence scg extraction. The mixed solvents were used to extract Forestburg subbituminous coal at 400° and 1900 psig (Table IV).

A. Polar Additives

Part of the bonding within the "coal molecule" is due to weak hydrogen bonding. Hydrogen bonding can be disrupted by using polar materials and therefore the addition of polar solvents could conceivably enhance the coal pyrolysis and increase the solvent power

of the solvent. The effectiveness of a number of polar solvents was tested by adding these to toluene at the five weight percent level.

1. Pyridine:

Pyridine ($T_c = 347^\circ$) is a coal specific solvent which will dissolve up to 40% of a coal under certain conditions. Its use as a co-solvent did not result in any reduction of the char yield at either the 5% or 25% level. The cdl isolated were more viscous than those normally isolated indicating that pyridine had a detrimental effect on the process.

2. N-Methyl-2-oxazolidone (Methyloxazolidone):

Methyloxazolidone is an example of a heterocyclic nitrogen containing compound with unique solvent properties for hydrocarbon as well as being completely miscible with water. Its use as a co-solvent did result in a lower yield of char (212 grams versus 221 grams for toluene) but the solvent completely decomposed under the extraction conditions. Therefore, the usefulness of this solvent is limited by its stability.

3. p-Cresol:

As a pure solvent, p-cresol ($T_c = 432^\circ$; $P_c = 50.8$ atm) did enhance the coal pyrolysis reaction but was unstable under the extraction conditions. As a co-solvent, p-cresol did not enhance the coal pyrolysis reaction (223 gram of char) but still underwent polymerization. This result shows the p-cresol has little use in the scg extraction of coal.

4. Anisole:

Anisole ($T_c = 369^\circ$; $P_c = 41.3$ atm) is an example of an aromatic ether. Use of this material did not result in decreased char yield (220 grams) and the solvent appeared to be unstable under the extraction conditions. This solvent also has little use as co-solvent in scg extraction methods for coal.

5. Tetrahydrofuran (THF):

Tetrahydrofuran is an example of an aliphatic (naphthenic) ether and could also be considered as a hydrogen donating solvent. Use of the material as co-solvent did not significantly enhance the coal pyrolysis reaction (217 grams char) but did increase the yield of cdl isolated (66 grams compared with 56 grams for toluene alone). There was no evidence suggesting that THF either polymerized or acted as a hydrogen donating solvent (furan was not detected). The enhanced cdl isolation suggests addition of THF increases the solvent power of toluene for cdl.

B. Free Radical Initiators

The pyrolysis of coal is a process which proceeds primarily via free radical mechanisms. The addition of free radical initiators to toluene at the one and two weight percent level was studied to determine if the coal pyrolysis reaction would be enhanced. The initiators chosen for study were:

cumene which forms a stable tertiary benzyl radical by homolysis

of a carbon-hydrogen bond;

3,4-dimethyl-3,4-diphenylhexane which forms a stable tertiary benzyl radical by homolysis of a carbon-carbon bond;

t-butyl peroxide, which is a common free radical initiator and one of the very few peroxides having a measurable half-life at 400°, forms a t-butoxy radical by homolysis of the oxygen-oxygen bond. None of these initiators enhanced the pyrolysis of the coal. All increased the yield of bibenzyl showing that the initiators initiated free radical reactions in the solvent leading to solvent degradation. Free radical initiators do not play a desirable role in the scg extraction of coal.

C. Hydrogen Donating Solvents

Coal is a hydrogen deficient material. The addition of hydrogen, either directly or by way of a hydrogen donating solvent, greatly enhances coal conversion to liquid products. Although tetralin is known to be an effective hydrogen donating solvent, two other possible hydrogen donating solvents, indane and decalin were tested in order to gain a better understanding of the properties of a useful hydrogen donating solvent.

1. Indane:

The use of this co-solvent lead to some reduction in char yield. Indane proved to be about 1/5 as effective as tetralin.

2. Decalin:

The use of a mixture of cis and trans-decalin ($T_c = 408 - 418^\circ$;

Pc = 28.7 atm) did not result in reduction of char yield. Naphthalene, the expected product of hydrogen donation, was not observed by gas chromatographic analysis of the isolated cdl. Both observations show that decalin did not act as a hydrogen donating solvent.

3. Tetralin:

A series of extractions were carried out using various levels of tetralin ($T_c = 516^\circ$) in toluene. Tetralin reduced char yield and increased the cdl yield in every case. The reduction in char yield with increasing tetralin concentration is tabulated in Table V and plotted in Figure 1. The amount of cdl isolated increased in a corresponding manner. Little improvement in the degree of pyrolysis was achieved by increasing the concentration above 10%. The optimum level of tetralin for conversion will probably be between 5 to 10%.

The effect of increased donor solvent can be duplicated using a greater amount of solvent containing less donor solvent. For example, the same degree of coal pyrolysis (same char yield) was obtained by extracting one part coal with 11 parts solvent containing 10% tetralin as by extracting one part coal with 19 parts solvent containing 5% tetralin.

Most of the tetralin was recovered in all the extractions carried out with this co-solvent. Naphthalene is the product of tetralin dehydrogenation. Examination of the cdl as they are produced revealed

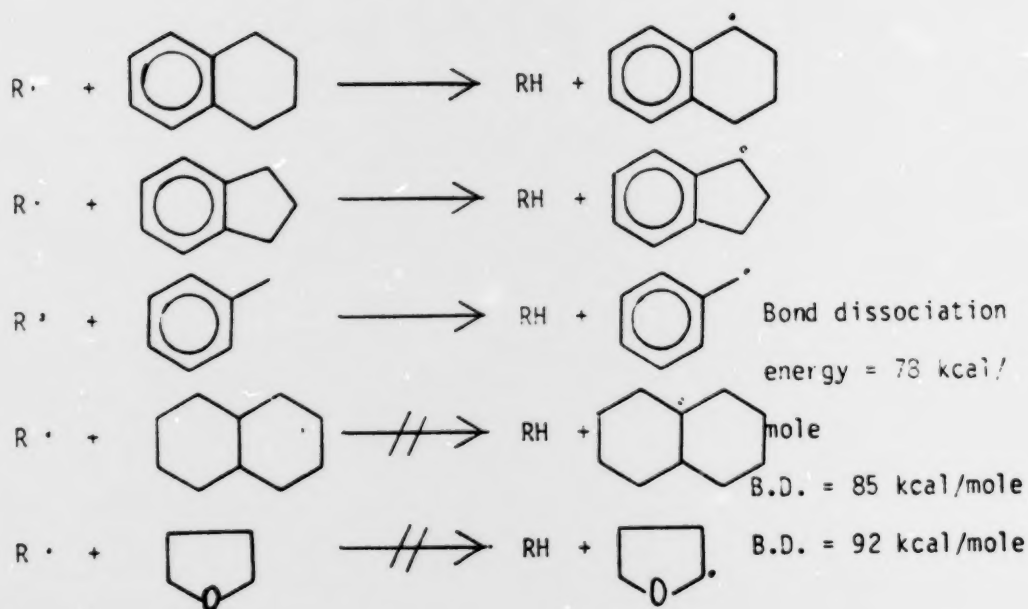
that naphthalene was not a product in the initial stages of the extraction (Table VI, Figure 2). Naphthalene appeared as a product when the extraction temperature reached 350 to 375°. The rate of naphthalene formation increased to a maximum at about 400° and then decreased as the formation of cdl decreased. The amount of naphthalene formed provides a measure of the amount of hydrogen entering into the pyrolysis reaction. Typically about one gram of hydrogen was donated.

In a separate experiment, it was shown that tetralin is stable under the temperature and pressure conditions of the extraction showing that hydrogen will be abstracted only when reactive coal derived radicals are present.

D. Conclusions

The pyrolysis of coal proceeds by free radical mechanism. Hydrogen abstraction is the most common reaction that radicals undergo. Hydrogen transfer occurs either as a principal reaction or as an unavoidable side reaction in almost every radical system. The radicals formed during coal pyrolysis are relatively stable radicals and therefore are selective. Selective radicals will only abstract hydrogen from the "weakest" carbon-hydrogen bond. A number of hydrogen abstraction reactions are shown in the scheme below.

Scheme 1



It would appear from our results that an effective hydrogen donating solvent must have an abstractable hydrogen for which the bond dissociation energy is less than 80 kcal/mole.

The rate of the hydrogen abstraction reaction can be influenced by the concentration of the hydrogen donating solvent. Therefore higher concentrations of tetralin will increase the yield of pyrolysis product. The coal derived radicals, however, are stable enough at 400° that lower concentrations of tetralin but larger solvent to coal ratios will achieve the same degree of pyrolysis. Toluene will act as a hydrogen donating solvent in the absence of a more effective solvent as

shown by the formation of bibenzyl.

The observation that decalin does not act as a hydrogen donating solvent may explain the observation that over-hydrogenation of recycled donor solvent leads to an ineffective hydrogen donating solvent. Complete hydrogenation of naphthalene leads to decalin, an ineffective hydrogen donating solvent.

E. Synthetic Solvents

The work performed at Raylo suggests that an effective solvent for scg extraction of coal should have some or all of the properties listed below.

1. The solvent should have a critical temperature near the temperature at which extraction is to take place. This will ensure that the supercritical gas will be dense at the extraction temperature. A dense gas has more solvent power for cdl as can be seen from the results obtained in scg extraction using n-heptane and n-decane (1). This conclusion was also reached by British workers at the NCB.
2. An effective solvent must have aromatic content as shown by the results of toluene and paraffinic solvent extractions. The solvent power of aromatic solvents for cdl is greater than the solvent power of paraffinic solvents for cdl.
3. Hydrogen donating solvents up to 5 to 10% "tetralin equivalent" drastically increases the extent of coal pyrolysis and the yield of isolated cdl.

4. The solvent power of the solvent may be increased by polar THF like solvents.

F. Alternative Solvents

With the above criteria in mind, an attempt was made to identify some industrial solvents which could be used for scg extraction. Attempts were made to procure Shell TS-28 or TS-28R (b.p. 168 - 200°; 73 - 75% aromatic, 10 - 14% naphthenic, 13 - 15% paraffinic) or Solv Esso 100 (b.p. 155 - 173°; 98.9% aromatic, 1.1% paraffinic). However these solvents were only available in drum quantities.

1. Extraction with Varsol:

Varsol is a very common industrial solvent sold by Esso. This material has a boiling point range of 150 - 181° and has an aromatic content of 19% and a paraffinic content of 81%. Extraction of 400 grams of Forestburg subbituminous coal at 400° and 1900 psig resulted in 217 grams char (Table VII). The solvent was not removed to isolate the cdl. Instead, the Varsol containing cdl was recycled and used to extract a fresh batch of subbituminous coal. The char yield of the second extraction using "recycled" solvent was 219 grams indicating that the addition of a small amount of cdl did not "improve" the solvent significantly. The solvent was removed to leave 105 grams cdl, and average of 52.5 grams for each extraction. This compares very favourably with 56 grams toluene extraction under the same conditions.

The extent of coal pyrolysis and the isolated yield of cdl shows that Varsol is as good a medium as toluene for scg extraction of subbituminous coal. This was unexpected in view of the relatively low aromatic content of the solvent.

The extraction was repeated using five percent tetralin in Varsol. The results show that this solvent mix is not as effective as five percent tetralin in toluene. Possibly, the aromatic content of Varsol represents the lower limit of aromatic content for an effective scg extraction solvent. Varsol by itself is as effective a solvent as toluene. However, when a hydrogen donating solvent is added, the increased yield of cdl is not as effectively dissolved resulting in lower isolated yields of cdl and possibly the formation of secondary products resulting in some redeposition and consequently larger amounts of char. If a hydrogen donating solvent is present the aromatic content of a scg extraction solvent should be greater than 25%.

2. Extraction with Naphtha:

A five gallon sample of "Plant A" naphtha was obtained from Syncrude courtesy of Dr. Emerson Sanford. This material had a boiling point range of 70 to 135°. The material had some aromatic content as determined by nmr spectroscopy. Extraction of 400 grams subbituminous coal led to 234 grams char and 45 grams cdl (Table VII). This solvent was not as effective as Varsol.

The extraction was repeated using 5% tetralin in naphtha. The char yield changed substantially while the cdl yield appears to be too low.

These results confirm that an effective scg extraction solvent must have aromatic content.

IV. HIGH TEMPERATURE-HIGH PRESSURE EXTRACTION APPARATUS

A. Assembly and Commissioning of the Apparatus

1. The Autoclave:

Figure 3 shows a full scale drawing of the autoclave designed and constructed by Pressure Products Industries of Warminster, Pennsylvania. The vessel has a capacity of 150 millilitres with design temperature of 600° and design pressure of 6000 psi. The autoclave, constructed of 316 stainless steel, weighs about 32 pounds.

2. The Apparatus:

Figure 4 shows a schematic diagram of the assembled apparatus. The liquid feed pump is a Bran and Luebbe model NP-31 with a 5 mm plunger capable of producing 5700 psi at flow rates fully adjustable from 0 to 48 millilitres per minute (0.73 USGPH). The pressure gauges are Hydro-Poise series No. 801 graduated from 0 to 5000 psi (0 - 35 MPa). The Bourden tube and all metal parts are constructed of 304 stainless steel. The three valves are Sno-Trik 1/4 inch FP valves capable of withstanding pressures of up to 45,000 psi at room

temperature. The stem packing is asbestos-inconel capable of withstanding temperatures in excess of 600°. The heated tubing consists of 1/4 inch O.D. 0.095 inch wall thickness annealed 316 stainless steel (30,000 psi at room temperature) connected with Sno-Trik high pressure fittings. All other tubing consists of 1/4 inch O.D. 0.065 inch wall thickness 316 stainless steel connected with Swagelok fittings.

The temperature bath is a Tecam TC-101 fluidized bath capable of reaching temperatures up to 600°. The lifting device is a Strongarm hydraulic automobile jack with a straight-up lift of 22 inches.

3. Commissioning:

The initial commissioning run was performed using toluene. The object was to control the pressure at 2500 psi with a liquid feed rate of about 20 millilitres per minute as the temperature rose from near room temperature to a final temperature of 400°C. Secondary objects were to determine the rate of heating and the ease of pressure control.

The temperature of the bath was raised to 475° while it was in the down position. When this temperature was reached, the temperature controller of the bath was reset to 400°, the pump was started and pressure was controlled with valve 1 (Fig. 4) at 2500 psig. At this stage the fluid flowing is a liquid so the pressure can only be controlled to $\pm 10\%$. The bath is then raised to immerse the pressure

vessel in the hot fluidized material. The resulting pressure increase was controlled by valve 2 (Fig. 4) which is in parallel with valve 1 and acts as a trimmer valve. Even during the period the temperature was rising rapidly, the pressure was very easily controlled and could be maintained within $\pm 1\%$ of the desired value after the supercritical temperature of toluene was reached.

Figure 5 shows the decrease in bath temperature and the increase in internal autoclave temperature during the run. This data shows that 320° (80% of set point temperature) was reached within nine minutes from the start of heating, 360° (90%) was reached within ten minutes and the desired temperature was reached in 16 minutes. The desired set point temperature was exceeded by 10° .

To round out the commissioning trial, the pressure was increased to 4500 psig and the liquid feed rate was increased to 40 millilitres per minute. Pressure control to within $\pm 1\%$ could be maintained under these conditions. The trial was terminated by lowering the fluidized bath, releasing the pressure and stopping the pump.

The inaugural trial was successful since the desired fast heating rate was achieved and pressure control could be readily maintained. However, during both the heating and cooling cycle, small leaks developed in the system. Leakage was especially apparent at the solvent inlet and at the gasket between the cover and the body of the autoclave. These difficulties required modification of the equipment.

4. Equipment Modifications:

The leakage associated with the solvent inlet was reduced by replacing the two piece inlet fitting (Figure 3) consisting of a 17-4-PH bayonet filter seat and a high pressure tube fitting with a one piece 316 SS combined bayonet filter seat - 1/4 inch tube stub. A copper gasket was placed between the filter seat and the autoclave body to eliminate the stainless steel to stainless steel butt joint. Occasionally, leakage still occurred during the heat-up cycle but this could be controlled by tightening the seat retaining nut.

Leakage between the body and the cover was eliminated by refacing the joint-face of the autoclave body removing a shallow groove designed to take the gasket. Indications were that the shallow body groove did not match up with a deeper groove in the cover. The annealed 316 SS gasket supplied by the manufacturer (\$107 each) was replaced with a locally manufactured copper gasket (\$7 each). These modifications eliminated leakage between the body and the cover.

B. Extractions of Coal

The results of a number of successful extractions of 70 grams of Forestburg subbituminous are summarized in Table VIII. The following observations can be made.

1. The yields of cdl for extractions at similar pressures and temperatures are independent of the apparatus used (compare Tables VIII and IV).
2. Decreasing the heat-up time from about 90 minutes to 10 minutes to reach 90% of the set point temperature has little or no effect on the yield of cdl or char.
3. The solvent to coal ratio has very little effect on the yield of cdl at extraction temperatures in excess of 400°.
4. The amount of solvent passed through the coal (solvent to coal ratio) does have a significant effect on cdl yield at extraction temperatures less than 400°.
5. Pressures in excess of 3000 psig leads to marginally increased yields of cdl. The increase yield is not nearly as great as predicted by the empirical formula:
$$Y = -72.1395 + 11.9 (^\circ K/100) + 6.375 (\text{psig}/100)$$
derived from a series of extractions performed at pressures ranging from 1100 to 1900 psig and temperatures ranging from 350 to 450° using the original extraction equipment.
6. Extraction with toluene at 500° led to abnormally large amounts of cdl. This is indicative of solvent polymerization.

The first observations justify the application of the results of a mathematical analyses of data obtained by the use of the low temperature-low pressure apparatus, to the data obtained by the high

temperature-high pressure apparatus. Increasing pressure from 1100 psig to 1900 psig has a very significant effect on the isolated yield of cdl. The pressure effect becomes less pronounced at pressures beyond 2000 psig as shown by the discrepancy between actual yield and calculated yield. This discrepancy becomes very large for extractions at 4500 psig, the extraction at 4500 psig and 500°C excepted for the reason already stated. These results show that high pressures are not warranted in the scg extraction process.

Analysis of the original data (1) suggested that the extraction efficiency, defined as the observed yield of cdl divided by a hypothetical yield, derived from thermogravimetric analysis, increased from 0.65 at 1100 psig to 0.87 at 1900 psig. Since the extraction efficiency was found to be linearly dependent on pressure and independent of temperature, complete extraction efficiency would be achieved at relatively low pressure. Using the empirical formula for extraction efficiency ($S = 0.3459 + 0.2772 P/1000$), complete extraction efficiency would be achieved at 2360 psig. The data in Table VIII suggests that the optimum pressure for supercritical toluene extraction lies in the 2000 to 3000 psig range. Increasing pressures to 4500 psig results in only marginal improvements in the isolated cdl yield.

Solvent to coal ratios have very little physical meaning in the semi-continuous extraction mode since the ratio is entirely dependent on the volume of the autoclave, the extraction temperature and

pressure. The solvent to coal ratio in the reaction zone is essentially constant at any given temperature and pressure. In the semi-continuous mode, the solvent to coal ratio is only a measure of the units of solvent passed per unit of coal. The ratio has no effect on the isolated yield of cdl at extraction temperatures of 400° or more. The ratio has a significant effect at 380° indicating that the rate of coal pyrolysis is the limiting factor in the scg extraction process. The data indicates that the rate of pyrolysis is significantly greater at 400° than it is at 380°.

C. Continuous Sampling of a Toluene Extraction

The above results indicated that some valuable data could be obtained by monitoring the yield of cdl as the temperature increased.

Forestburg subbituminous coal (70 grams) was heated from 20 to 560°C at 3000 psig while toluene was pumped through the coal at a liquid feed rate of 6.8 grams per minute. Samples were taken at every 20 degree rise in temperature. The results are shown in Table IX. The rate of extraction, expressed as grams cdl per 1000 grams of toluene pumped against temperature is plotted in Figure 6.

The results show that the rate of extraction remains low between 20 to 340° with a maximum in the 160 to 220° range. The extraction rate increases dramatically after 340°. The formation of bibenzyl is noted at this point. The extraction rate peaks between 400 - 420°, declines to 440° and increases again at higher temperatures.

These results show a number of distinct changes during the extraction process. The cdl extracted in the 20 to 340° range (2.6 grams) are hydrocarbons already present in the coal or moieties readily split from the coal "molecule" which are more efficiently dissolved in toluene as the temperature increases. The nmr spectra indicate that these materials are primarily paraffinic and naphthenic in nature with essentially only paraffins being extracted up to 120° and naphthenic material appearing after 120° (absorbance in the 2 to 3 ppm range). Traces of aromatic material appear after 80°.

From 340 to 440° (5.3 grams cdl) active coal pyrolysis takes place. This is indicated by the increased rate of extraction and by the appearance of bibenzyl in the extract. Coal pyrolysis proceeds via free radical mechanisms. The free radicals formed can abstract hydrogen from toluene which can couple with another benzyl radical to form bibenzyl. The active pyrolysis conclusion is supported by the results of extraction in the presence of tetralin. Naphthalene formation is noted at temperatures exceeding 350°. The conclusion is further supported by thermogravimetric analysis results which indicate rapid weight loss in this temperature range.

The most rapid extraction rate occurs between 400 to 420° indicating that this range is the optimum temperature range for supercritical toluene extraction of this particular coal.

The extraction rate again increases after 440°C. Thermogravimetric analysis indicates that there should not be an increase in thermolysis rate at this stage. The increased extraction rate indicates that the extraction solvent is starting to thermally polymerize. This temperature effectively defines the temperature limit for supercritical toluene extraction.

The nmr data shows that the relative yield of bibenzyl decreases at temperatures beyond 500°. The ratio of aromatic and phenolic hydrogen to total hydrogen (Ha) increases steadily after the start of active coal pyrolysis.

The total amount of water isolated was 10.4 grams. The lower than expected yield could be due to losses caused by frequent sampling. Traces of moisture appeared in the 120 to 140° range while the bulk of the water was released in the 260 to 320° range. This experiment does not allow differentiation between surface water and chemically formed water.

This experiment affords an effective method for determining the stability of solvents at elevated temperatures in the presence of pyrolysing coal. The suitability of a solvent as scg extraction medium can be determined in a single experiment.

V. CONCLUSIONS

Some major conclusion can be drawn from the data obtained during this contract period.

1. An effective scg extraction solvent for subbituminous coal should have the following properties:

- at least 30% aromatic content;
- hydrogen donating capacity of 8 - 10% "tetralin equivalent";
- potential hydrogen donating compounds should have an abstractable hydrogen having a bond dissociation energy of less than 80 kcal/mole.

The solvent power of the scg extraction solvent can be enhanced by the addition of THF and possibly by the addition of aromatic ethers.

An effective scg extraction solvent should not have phenolic compounds or nitrogen containing compounds.

The experimental methods described can be readily adapted to determine the make-up of a suitable scg extraction solvent for any coal.

2. The optimum temperature for scg extraction of subbituminous coal with toluene as base solvent lies in the 400 to 420° range. The rate of cdl extraction is limited by the rate of coal pyrolysis at temperatures below this range while rate of thermal degradation of the solvent becomes excessive at temperatures above this range. The methods for determining the optimum temperature range are readily applicable for any coal-solvent combination.

3. The optimum pressure for scg extraction lies in the 2300 to 3000 psig range. Both optimum pressures and temperatures could be better defined by carrying out a factorial set of extractions studying these two variables at three levels.
4. Meaningful data on two other potentially important variables, solvent to coal ratio and residence time, cannot be obtained by carrying out extractions in the semi-continuous mode. These can be obtained using a fully continuous method of extraction. Obtaining meaningful data on these two variables is necessary before a pilot plant having a reasonable chance of success can be designed. This data is necessary before an economic assessment of the process can be obtained.

VI. ANALYSIS OF CDL

Pooled cdl from supercritical toluene extractions of Forestburg subbituminous coal sample 1 at 350 to 450° and 1100 to 1300 psig was analyzed using standard methods.

A. Solvent Analysis

Solvent analysis is a method frequently used to characterize the liquid products obtained from coal liquefaction processes. Samples are separated into fractions according to their solubilities in several

solvents. The solvent analysis scheme employed separates the cdl into four main groups; oil (pentane soluble), asphaltene (toluene soluble, pentane insoluble), preasphaltene (THF soluble, toluene insoluble), and insoluble residue. It should be noted that all of the above materials are soluble in supercritical toluene.

1. Distillation:

The cdl were heated to $200 \pm 10^\circ$ at atmospheric pressure prior to separation into the various fractions. This ensures that the cdl are process solvent free.

2. Separation into Toluene Soluble and Insoluble Material:

The method used was outlined by Mima et al (2). About ten grams of distillation residue was slurried with 20 millilitres toluene. The toluene slurry was filtered through a tared Soxhlet thimble into a round bottomed flask. The solid residue was extracted with toluene for 24 hours using a Soxhlet extraction apparatus. The thimble was dried and the weight of the toluene insoluble material recorded.

The toluene was removed by rotary evaporation, the residue dried under one Torr vacuum and the weight of the toluene soluble material was recorded.

3. Separation into Preasphaltene and THF Insoluble Material:

The toluene insoluble material was not removed from the Soxhlet thimble. The thimble was replaced in the Soxhlet apparatus and extracted with THF for two hours. The thimble was dried and the weight

of the THF insoluble material recorded (Table X).

The THF was removed by rotary evaporation, the residue dried and the weight of the preasphaltene recorded (Table X).

4. Separation into Oil and Asphaltene:

The method used was described by Steffgen et al (3). The toluene soluble material obtained above was redissolved in toluene using a solvent to cdl ratio of three millilitres per gram. Pentane was rapidly added to the vigorously stirred solution using a pentane to toluene ratio of 20 millilitres per millilitre. The precipitated solid was collected by filtration through a tared Soxhlet thimble and extracted with pentane for 24 hours using a Soxhlet apparatus. The Soxhlet thimble was dried and the weight of asphaltene recorded (Table X). The pentane was removed, the residue dried and the weight of oil (maltene) recorded (Table X).

B. Separation of Asphaltene into Acidic/Neutral and Basic Fractions

A fractionation method described in the literature (4) was used. The method involved redissolving the asphaltene in toluene. Typically a portion of the asphaltene does not redissolve. This is probably due to the removal of oil which alters the solvent power of the solvent for asphaltene. The undissolved solid (about 2% of the total solids) were removed and the solution was treated with dry hydrogen chloride gas. The precipitated salts were collected and suspended in fresh toluene and treated with a 0.3 molar solution of sodium hydroxide to convert

the salts into basic asphaltene. The toluene was removed to isolate the basic material (Table X).

The acidic/neutral asphaltene remained in solution when the solution was treated with hydrogen chloride gas. These were isolated by removal of the toluene (Table X). The total recovery of asphaltene was about 84%. Amphoteric asphaltene would be lost in the described procedure and it is expected that this probably accounts for the loss of material.

C. Liquid Chromatography

The oil obtained from the solvent analysis was separated into saturated, aromatic and polar material by liquid chromatography. A dual packed silica gel-alumina column was prepared using the same quantities of equivalent materials activated as prescribed by Sawatzky et al (5). A weighed quantity of oil was eluted from the column using the elutropic order, quantities and flow rate of solvents specified. The eluent was collected in ten millilitre fractions. A thin layer chromatography (tlc) method was developed to determine which fractions could be pooled. The solvent was removed from the pooled fractions and the weights of the materials were recorded (Table X).

Tlc showed that two distinct classes of compounds were eluted with pentane. Proton nmr showed that the first fraction contained very little aromatic/phenolic protons. The second fraction contained aromatic protons. Tlc also showed that relatively clean separations were obtained throughout the elutropic sequence.

The data in Table X shows that the bulk of the oil (32%) is eluted

with methanol/benzene/ether. This is polar material.

D. Elemental Analysis; Molecular Weight and NMR Data

Table X records the elemental analysis, average molecular weight (by vapour phase osmometry) and nmr data for fractions of cdl obtained by the above procedure. The data shows that the elemental hydrogen to carbon ratio increases from 0.85 for the THF insoluble material, to 0.96 for the preasphaltene, to 0.99 for the total asphaltene to 1.37 for the total oil. All of these values are higher than the H/C ratio for the original coal (0.78). The elemental oxygen to carbon ratio decreases from 0.17 for the THF insoluble material to 0.14 for the preasphaltene to 0.12 for the asphaltene to 0.06 for the oil. All these values are lower than the O/C ratio for the original coal (0.18). The sulfur content is generally lower than that of the coal.

The average molecular weight of the total oil shows that this material is relatively light. The oil molecule contains about 18 carbon atoms, 25 hydrogen atoms and one oxygen atom. Every tenth molecule will contain a nitrogen atom while every twentieth molecule will contain a sulfur atom. Similarly the polar oil molecule will contain about 18 carbon atoms, 23 hydrogen atoms and two oxygen atoms. Every fifth molecule will contain a nitrogen atom and every twenty-fifth molecule will contain a sulfur atom.

The elemental analysis of the basic/neutral and acidic asphaltene shows that the nitrogen content is very similar for both materials.

The oxygen content for the basic material is much greater than it is for the acidic/neutral asphaltene.

The aromatic and phenolic hydrogen to total hydrogen ratio (H_a) obtained by integration of the proton nmr spectrum suggests a low amount of unsaturation. The asphaltene fraction is the most highly aromatic portion of the cdl. The amounts of carbon, hydrogen and oxygen in the oil molecule suggest about six to seven unsaturations. A single aromatic ring represents four unsaturations. A naphthalene moiety represents seven unsaturations. The H_a value of 0.25 suggests the molecule contains six to seven aromatic or phenolic hydrogen atoms.

E. FTIR Data

Diffuse reflectance Fourier transform infrared spectra of THF insoluble material, preasphaltene and fractionated asphaltene were determined (Figures 7 to 10).

THF Insoluble Material:

Qualitatively, Figure 7 is very similar to the rest of the FTIR spectra. Figure 7 shows a strong absorbance at 3200 cm^{-1} associated with hydrogen bonded O-H or N-H stretch, a weak absorbance at 3050 cm^{-1} indicative of aromatic C-H stretch, three absorbance bands at 2880 , 2920 and 2960 cm^{-1} associated with C-H stretching in methyl and methylene groups, a weak absorbance at 1700 cm^{-1}

associated with carbonyl stretch, a strong absorbance at 1600 cm^{-1} probably associated with enhanced aromatic ring resonance due to -OH substitution (6), an absorbance band centered at 1460 cm^{-1} associated with aliphatic C-H bending, a weak absorbance at 1380 cm^{-1} associated with methyl C-CH₃ bending, absorbance between 1200 to 1300 cm^{-1} associated with ether linkages or phenolic O-H bending and a number of absorbance bands appearing in the 740 to 900 cm^{-1} range associated with aromatic C-H bending. The sharp absorbance at 700 cm^{-1} is generally associated with CH₂ rocking when several methylene groups are linked together. The combination of this absorbance with the absorbance band in the 740 to 760 cm^{-1} range could also be indicative of benzyl substitution. This possibility should be explored for it could form the basis of an analytical method for toluene substitution in the cdl and char remaining after supercritical toluene extraction.

2. Preasphaltene:

The FTIR spectrum of preasphaltene (Figure 8) shows the same absorbance bands as the spectrum of the THF insoluble material. The relative intensities of the absorbance bands vary. The band at 700 cm^{-1} is much more intense in Figure 8 than it is in Figure 7.

3. Acidic/Neutral Asphaltene:

Figure 9 is very similar to Figures 7 and 8. The main difference between these spectra are the relative intensity of each absorbance

band. The absorbance band at 1700 cm^{-1} is indicative of some carboxylic acid carbonyl stretching. The position of this absorbance band suggests the presence of acetic acid residues rather than benzoic acid residues. This absorbance band could also be associated with cyclic ketone carbonyl stretching.

4. Basic Asphaltene:

The spectrum of the basic asphaltene (Figure 10) is very similar to the previous spectra showing only a difference in the relative intensity of the absorbance bands. The band at 700 cm^{-1} is very intense. There is a residual absorbance in the carbonyl region.

VII. ANALYSIS OF CHARS

A, Proximate Analysis and Calorific Value

Table XI summarizes the proximate analysis and calorific values of chars derived from extraction of Forestburg subbituminous coal sample 1 with various solvent mixtures. The analysis of the char derived from pyridine-toluene and tetralin-toluene (solvent to coal ratio 16.5) are the same. The analysis of the char from tetralin-toluene (solvent to coal ratio 10.0) is significantly different from the above chars.

Decreases in calorific value relative to the coal are noted for the pyridine-toluene and tetralin-toluene (solvent to coal ratio 16.5) extractions while a slight increase in calorific value is noted for the

low solvent to coal ratio tetralin-toluene extraction. The increase is significant for the toluene extraction.

The yields of char and cdl are also tabulated. Although the char and cdl yields for toluene extraction and pyridine-toluene extraction are very similar, the proximate analysis of the chars are very different. The proximate analysis and calorific value for the high solvent to coal ratio tetralin-toluene extraction and the pyridine-toluene extraction are the same but the yields of char and cdl are very different. These results show extraction with pyridine alters the properties of the coal considerably but does not result in increased yields of cdl. The cdl from pyridine extractions were observed to be very viscous.

B. Petrographic Analysis

Chars derived from Forestburg subbituminous coal extracted with various levels of tetralin in toluene were submitted for petrographic analysis. The overall results show there is not a great deal of difference in the nature of the chars. The samples extracted with tetralin present are slightly more altered than the sample obtained from extraction with toluene alone. There does not appear to be any correlation between the nature of the chars and the amount of tetralin in the extraction medium even though there was a definite correlation between yield of char and level of tetralin used in the extraction medium.

There was no evidence for any coke formation nor for redeposition of coal derived materials on the char. This is significant since a previous sample derived from an extraction in which the coal was heated with tetralin prior to extraction with supercritical toluene did show the formation of significant amounts of semi coke. This observation shows that it is important to remove cdl from the reaction zone to prevent coking and possible fouling of the extraction equipment.

The report of the petrographic study, performed by Mrs. J. Potter at the University of Regina, is attached as an Appendix to this report.

VIII. REFERENCES

1. "Optimization, Chemistry and Product Analysis of Supercritical Gas Extraction Techniques for the Liquefaction of Canadian Coals", Raylo Final Report, March 20, 1981.
2. M.J. Mima, H. Schultz and W.E. McKinsty, "Analytical Methods for Coal and Coal Products", C. Karr, Jr., Ed., Vol. 1, p.557 (1978).
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4. B.C. Bockrath, C.L. Delle Donne and F.K. Schweighardt, Fuel, 57, 4 (1978).
5. H. Sawatzky, A.E. George, G.T. Smiley and D.S. Montgomery, Fuel, 55, 16 (1976).
6. P.R. Solomon, United Technologies Research Centre, East Hartford, unpublished results.

TABLE I

Comparison of the proximate analysis and calorific value of two samples of Forestburg subbituminous coal with the typical analysis for that coal.

Sample ^{a)}	Determined	Moisture	Ash	Volatile Matter	Fixed Carbon	BTu/lb
1	As rec'd	21.5	4.7	33.7	40.1	9,104
	Dry Basis	--	6.0	42.9	51.1	12,122
2	As rec'd	26.9	8.0	28.1	37.0	7,704
	Dry Basis	--	10.9	38.4	50.7	10,533
Typical ^{b)}	As rec'd	26.0	11.0	28.0	35.0	8,000
	Dry Basis	--	14.9	37.8	47.3	10,811

a) Sample 1 obtained December 1979; Sample 2 obtained May 1981.

b) Supplied by Luscar Ltd.

TABLE II

Comparison of the ultimate analysis of two Forestburg subbituminous coal samples.

<u>Sample</u>	<u>Determined</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O</u>	<u>H/C</u>
1	As rec'd	53.75	3.51	1.14	0.60	12.98	--
	Dry Basis	71.57	4.68	1.52	0.80	17.28	--
	daf	74.67	4.88	1.59	0.83	18.02	0.78
2	As rec'd	47.31	3.29	1.02	0.42	13.13	--
	Dry Basis	64.68	4.50	1.39	0.58	17.95	--
	daf	72.59	5.05	1.56	0.65	20.15	0.83

TABLE III

Supercritical toluene extraction of 400 grams of coal at 400°C and 1500 psig of two Forestburg coal samples.

Sample _____	Products		% cd1	% Material (a)
	<u>char</u>	<u>cd1</u>	<u>daf</u>	<u>Balance</u>
1 (b)	218	47.0	17.3	93.8
1 (b)	234	49.4	18.2	98.4
2 (b)	217	50.0	19.4	94.2
2 (c)	218	57.5	22.3	96.4

(a) Includes 110 g of water.

(b) 12 - 24 mesh particle size.

(c) Unsieved coal ranging in particle size of less than 1/8" to -200 mesh.

TABLE IV

Effect of additives to toluene in supercritical gas extraction of 400 grams Forestburg subbituminous coal at 400°C and 1900 psig.

Additive	% w/w	Char (g)	cdl (g)	% cdl daf	% Material ^{d)} Balance
None	--	221	56	21.7	97
Pyridine	5	222	47	17.3	95
	25	222	55	20.3	97
3-Methyloxazolidone ^{a)}	5	212	110	42.6	108
p-Cresol ^{a)}	5	221	131	50.8	116
Anisole ^{a)}	5	220	76.6	29.7	102
THF	5	217	65.8	25.5	98
Cumene ^{b)}	2	221	89	34.5	105
3,4-dimethyl-3,4- diphenyl hexane ^{b)}	2	229	80	31.0	105
t-Butylperoxide ^{b)}	1	219	91	35.3	105
Indane ^{c)}	5	215	86	33.6	103
Decalin ^{c)}	5	219	64	25.0	98

a) Solvent polymerization noted.

b) Bibenzyl is major product and is solvent derived.

c) Yield of cdl estimated by gc using n-decane as external standard.

d) Includes 110 grams water.

TABLE V

Effect of tetralin addition to toluene in supercritical gas extraction of 400 grams Forestburg subbituminous coal at 400° and 1900 psig.

<u>% Tetralin</u>	<u>Solvent to coal ratio</u>	<u>Products (g)</u>		<u>% cdl daf</u>	<u>% Material Balance ^{a)}</u>
		<u>Char</u>	<u>cdl</u>		
0	10.0	221	56	21.7	97
2	10.0	210	76 ^{b)}	29.7	99
5	10.8	196	83 ^{b)}	32.4	97
5	19.0	181	--	--	--
10	10.8	181	75 ^{b)}	29.3	91
15	11.5	176	80 ^{b)}	31.2	91

a) Includes 110 grams water.

b) Yield of cdl estimated by gc using n-decane as external standard.

TABLE VI

Extraction of 400 grams Forestburg subbituminous coal with five percent (w/w) tetralin in toluene at 400°C and 1900 psig. Total volume of solvent pumped was 7600 millilitres.

<u>Sample^{a)}</u>	<u>Naphthalene (g)</u>	<u>cdl (g)</u>
1	---	1.6
2	---	14.4
3	1.3	7.4
4	3.4	10.1
5	4.8	9.2
6	5.0	7.2
7	3.8	6.8
8	4.0	5.5
9	3.6	4.7
10	3.3	3.4
11	2.4	5.2
12	2.2	2.0
13	2.4	3.3
14	2.0	2.3
15	2.0	3.2
16	1.9	3.0
17	1.8	2.6
18	1.7	2.4
19	1.7	2.6
Residue	<u>1.4</u>	<u>4.1</u>
TOTALS	48.7	101.0

a) Sample 1, 300 - 325°; 2, 325 - 350°; 3, 350 - 375°; 4, 375 - 400°; 5 and following taken at 15 minute intervals, 420 ml of solvent pumped for each fraction.

TABLE VII

Extraction of 400 grams Forestburg subbituminous coal at 400° and 1900 psig using alternative solvents.

<u>Solvent</u>	<u>Products (g)</u>		<u>% cdl (daf)</u>	<u>% Material Balance</u> ^{a)}
	<u>Char</u>	<u>cdl</u>		
Toluene	221	56	21.6	97
5% Tetralin/Toluene	196	83 ^{b)}	32.4	97
Varsol	217	52.5	20.2	95
5% Tetralin/Varsol	204	78 ^{b)}	30.2	98
Naphtha	234	45	17.4	97
5% Tetralin/Naphtha	215	44 ^{b)}	17.0	92

a) Includes 110 grams water.

b) Estimated by gc using n-decane as internal standard.

TABLE VIII

Effect of various experimental parameters on the yield of coal derived liquids resulting from supercritical toluene extraction of 70 grams of Forestburg subbituminous coal at 400°C.

Pressure (psig)	Residence time (min)	Solvent (g) Coal (g) Ratio	Room Temp. to 360° (min)	Char	Products (g) CdI Water ^{b)}	% CdI (daf)	% CdI Calc. ^{c)}	% Material Balance
1900	7.1	8.7	10	43.4	8.9	(19)	20.1	102
1900	1.6	32.7	11	40.7	9.5	(19)	20.1	99
2000	2.1	18.6	12	40.2	9.3	17.5	20.7	96
2000	4.7	24.8	90	40.7	9.7	21.5	20.7	103
2000	2.0	43.3	92	39.8	8.6	16.0	20.7	92
3000	1.8	18.6	11	40.0	10.0	(19)	27.1	99
3000 a)	2.4	18.6	21	43.0	6.3	19	22.6	98
3000 a)	2.4	37.2	21	40.8	8.5	19	22.6	98
4500	2.9	18.6	15	38.8	11.8	(19)	36.6	99
4500	3.0	18.6	11	37.0	10.6	(19)	36.6	95
4500	12.0	18.6	11	35.9	10.6	(19)	36.6	94
4500	8.3	18.6	99	37.5	10.1	17.0	36.6	92
4500 a)	2.3	18.6	16	44.8	6.3	(19)	34.3	100
4500 d)	10.7	18.6	16	42.1	25.1	7.0	48.5	106

a) Maximum temperature reached is 380°C.

b) Numbers in brackets is assumed weight while unbracketed numbers is measured weight. Percent yield and recovery are based on numbers in this column.

c) Calculated from $Y = -72.1395 + 11.9 (^{\circ}\text{K}/100) + 6.375 (\text{psig}/1000)$.

d) Extraction carried out at 500°C.

TABLE IX

Continuous sampling at regular temperature intervals of a supercritical toluene extraction of 70 grams Forestburg subbituminous coal at 3000 psig and a toluene feed rate of 6.8 grams per minute.

Temp (°C)	cdl (g)	ll 0 (g)	Toluene (g)	gcdl/ 1000 g toluene	lla	%P	Bibenzyl %A ^a
20 - 40	0.1	---	125	0.8	0	---	---
40 - 60	0.1	---	40	2.5	-	---	---
60 - 80	0.1	---	37	2.7	0	---	---
80 - 100	0.1	---	30	3.3	0.09	---	---
100 - 120	0.1	---	30	3.3	0.06	---	---
120 - 140	0.2	tr	30	6.6	0.16	---	---
140 - 160	0.1	tr	30	3.3	0.16	---	---
160 - 180	0.2	tr	30	6.6	0.09	---	---
180 - 200	0.2	tr	27	7.4	0.08	---	---
200 - 220	0.2	0.3	30	6.6	0.14	---	---
220 - 240	0.2	0.8	34	5.9	0.12	---	---
240 - 260	0.2	1.0	37	5.4	0.12	---	---
260 - 280	0.2	1.8	44	4.5	0.11	---	---
280 - 300	0.2	2.0	44	4.5	0.10	---	---
300 - 320	0.2	2.0	48	4.2	0.15	---	---
320 - 340	0.2	1.5	48	4.2	0.15	---	---
340 - 360	0.5	1.0	44	11.3	0.20	tr	tr
360 - 380	0.9	tr	51	17.6	0.20	tr	tr

Table IX continued

Temp (°C)	cdl (g)	H ₂ O (g)	Toluene (g)	gcdl / 1000 g toluene	b) IIa	%P	Bibenzyl %A
380 - 400	1.3	tr	50	25.9	0.26	tr	tr
400 - 420	1.7	--	64	26.5	0.31	3	15
420 - 440	0.9	--	48	18.9	0.34	4	20
440 - 460	1.3	--	68	19.2	0.44	7	20
460 - 480	1.5	--	32	18.4	0.53	14	26
480 - 500	1.9	--	88	21.5	0.58	17	27
500 - 520	2.8	--	102	27.4	0.63	16	23
520 - 540	4.8	--	120	40.1	0.69	11	13
540 - 555	6.3	--	113	55.9	0.70	9	11
555 - 560	11.2	--	146	76.9	0.70	8	8

a) Contribution of bibenzyl paraffinic hydrogen (%P) to total paraffinic hydrogen and bibenzyl aromatic hydrogen (%A) to total aromatic hydrogen by nmr integration.

b) Corrected for bibenzyl.

TABLE X

Elemental analysis, nmr and vapour phase osmometry data for fractions of cdl derived from Forestburg subbituminous coal by supercritical toluene extraction.

Sample	% Yield	Elemental Analysis ^{a)}					H/C	O/C	I/a	VP ^{c)}
		%C	%H	%N	%S	%O ^{b)}				
THF insoluble	10.0 ^{d)}	75.11	5.32	2.22	0.77	16.58	0.85	0.17	--	--
Preasphaltene	10.0 ^{d)}	76.74	6.14	2.04	0.77	14.31	0.96	0.14	0.32	--
Asphaltene	24.1 ^{d)}	78.60	6.46	1.37	0.56	13.01	0.99	0.12	0.37	--
Basic asphaltene	31.6 ^{e)}	70.14	5.90	1.84	0.67	21.45	1.01	0.23	0.37	--
Acidic/Neutral asphaltene	50.0 ^{e)}	78.48	7.53	1.77	0.63	11.59	1.15	0.11	0.32	576
Oil	50.2 ^{d)}	82.64	9.46	0.47	0.54	6.89	1.37	0.06	0.25	267
Pentane A	15.2 ^{f)}	82.48	12.07	0.12	0.33	5.00	1.76	0.05	0.07	--
Pentane B	10.8 ^{f)}	86.01	9.07	0.17	0.60	4.15	1.27	0.04	0.3	--
5% Benzene/Pentane	5.5 ^{f)}	86.51	8.94	0.20	0.86	3.49	1.24	0.03	0.28	--
Benzene	6.7 ^{f)}	83.30	3.32	0.74	0.66	6.98	1.20	0.06	0.19	--
MeOH/Et ₂ O/Benzene 3:1:1	32.0 ^{f)}	78.60	8.25	1.04	0.48	11.63	1.26	0.11	0.25	282

a) Performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.

b) By difference.

c) Performed at University of Alberta

d) Fractionated by solvent analysis of cdl - percent of total cdl.

e) Fractionated by method described in Reference 4 - percent of total asphaltene.

f) Obtained by liquid chromatography of the oil following the procedure in Reference 5 - percent of total oil.

TABLE XI

Proximate analysis and calorific value of chars derived from supercritical gas extraction of 400 grams Forestburg subbituminous coal sample 1 at 400° and 1900 psig using various solvents.

Solvent	Products (g) Char	Solvent (g) Coal (g)	% Ash	% Volatile Matter	% Fixed Carbon	Btu/lb
Coal a)	--	--	6.0	42.9	51.1	12,122
Toluene b)	218	10.0	6.8	25.9	66.0	13,206
5% Pyridine/toluene	222	10.0	8.3	26.3	65.4	11,775
5% Tetralin/toluene	186	16.5	8.5	26.5	65.0	11,978
5% Tetralin/toluene	201	10.0	7.9	28.3	63.8	12,190

a) Dry basis.

b) Pressure 1500 psig.

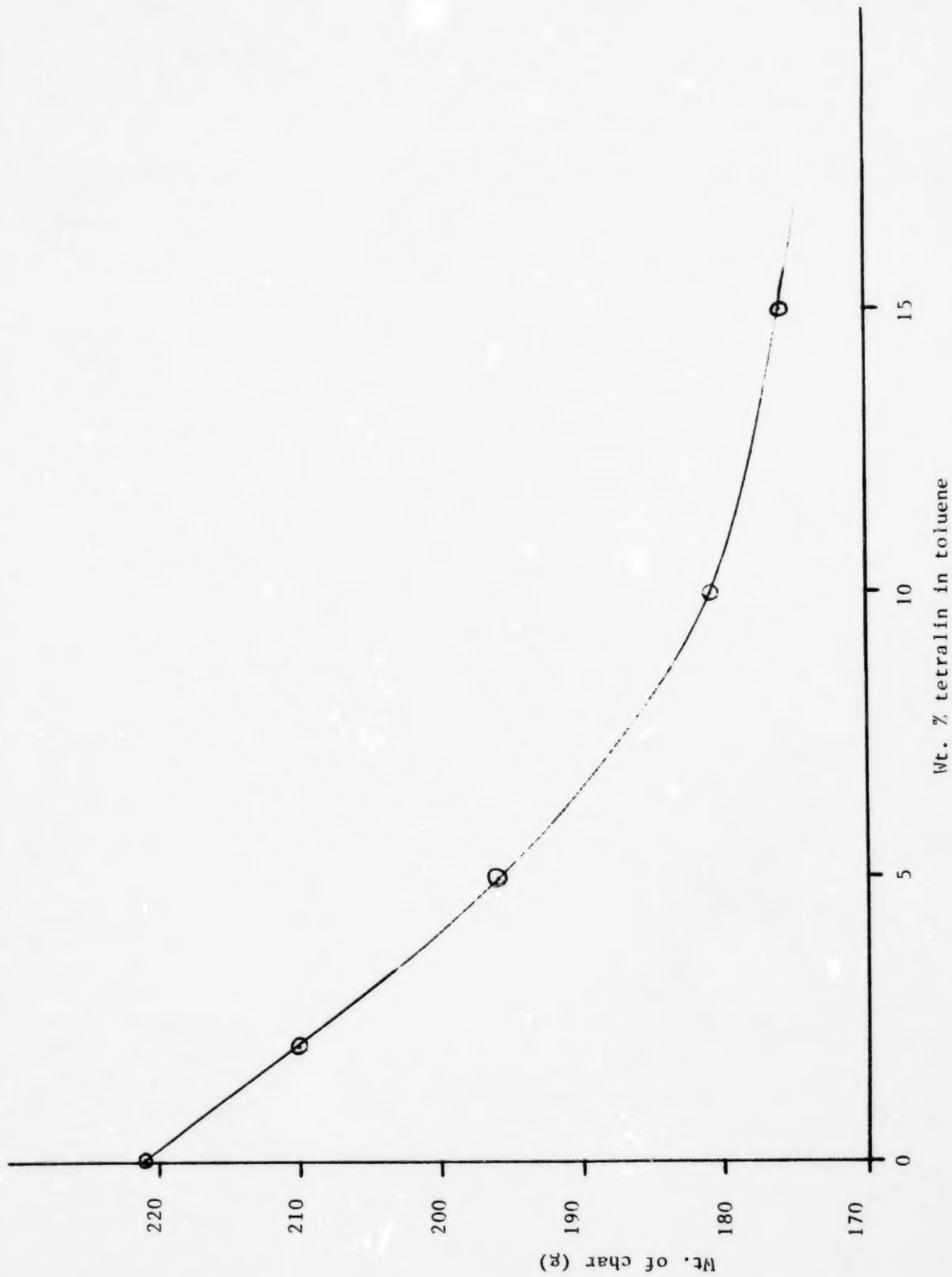


Figure 1: Effect of weight percent of tetralin in toluene on the amount of char remaining after supercritical extraction of 400 grams Forestburg subbituminous coal at 400°C and 1900 psig.

Figure 2: Relationship between the weights of cdl isolated and naphthalene formed during the extraction of 400 grams subbituminous coal at 400° and 1900 psig with 5% (w/w) tetralin in toluene

Legend

○ cdl

× naphthalene

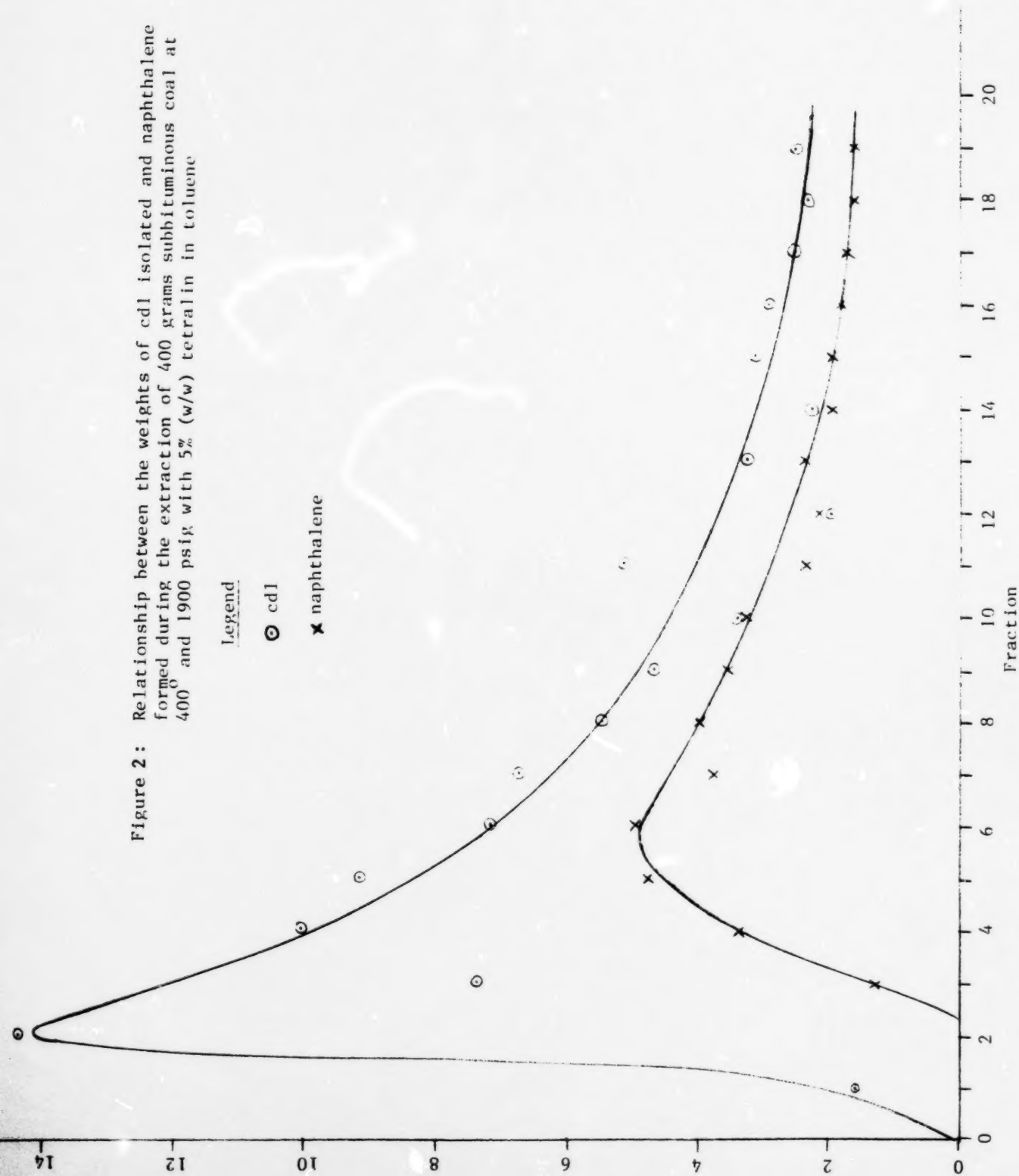
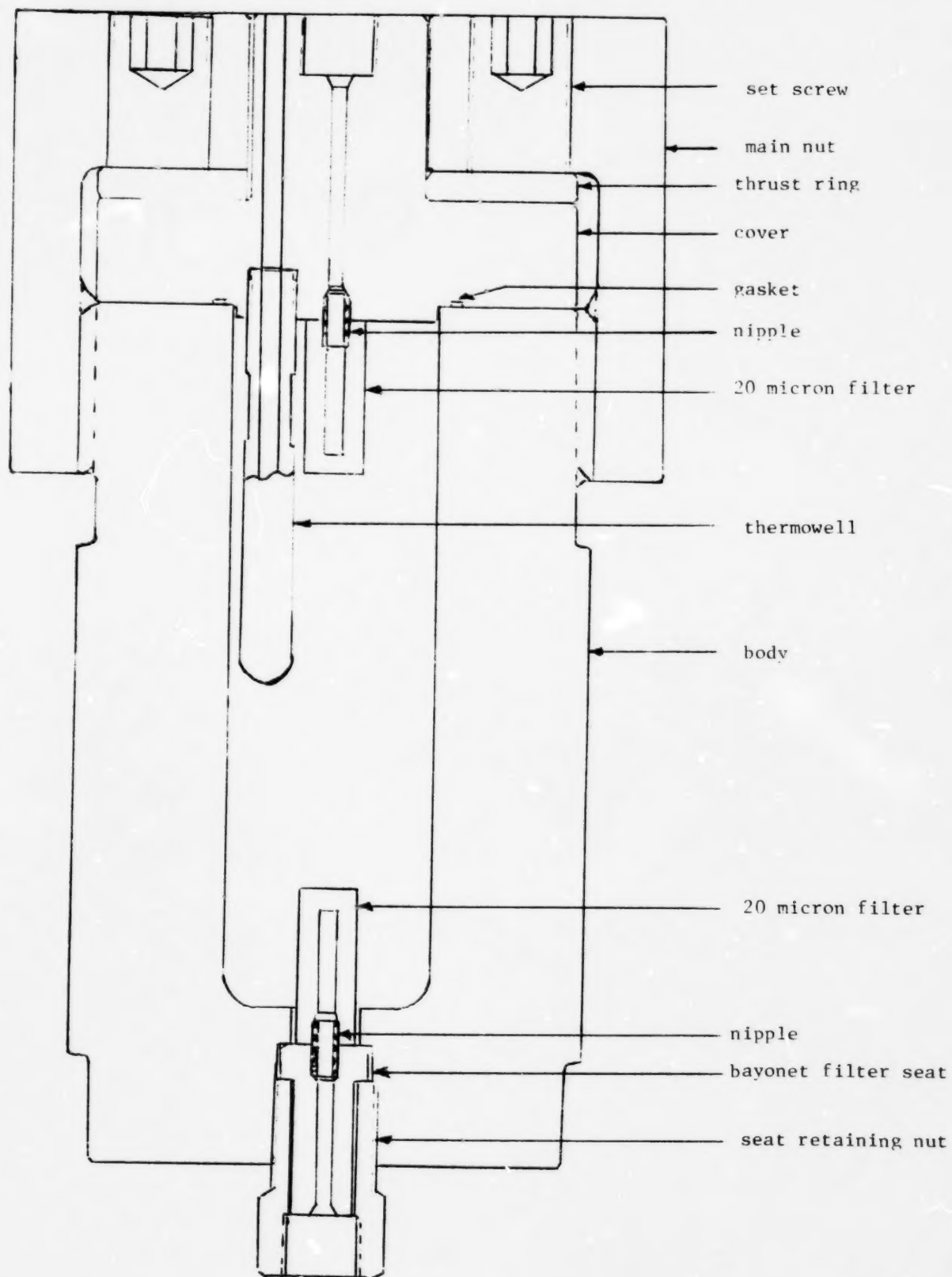


Figure 3: Full scale diagram of reactor assembly



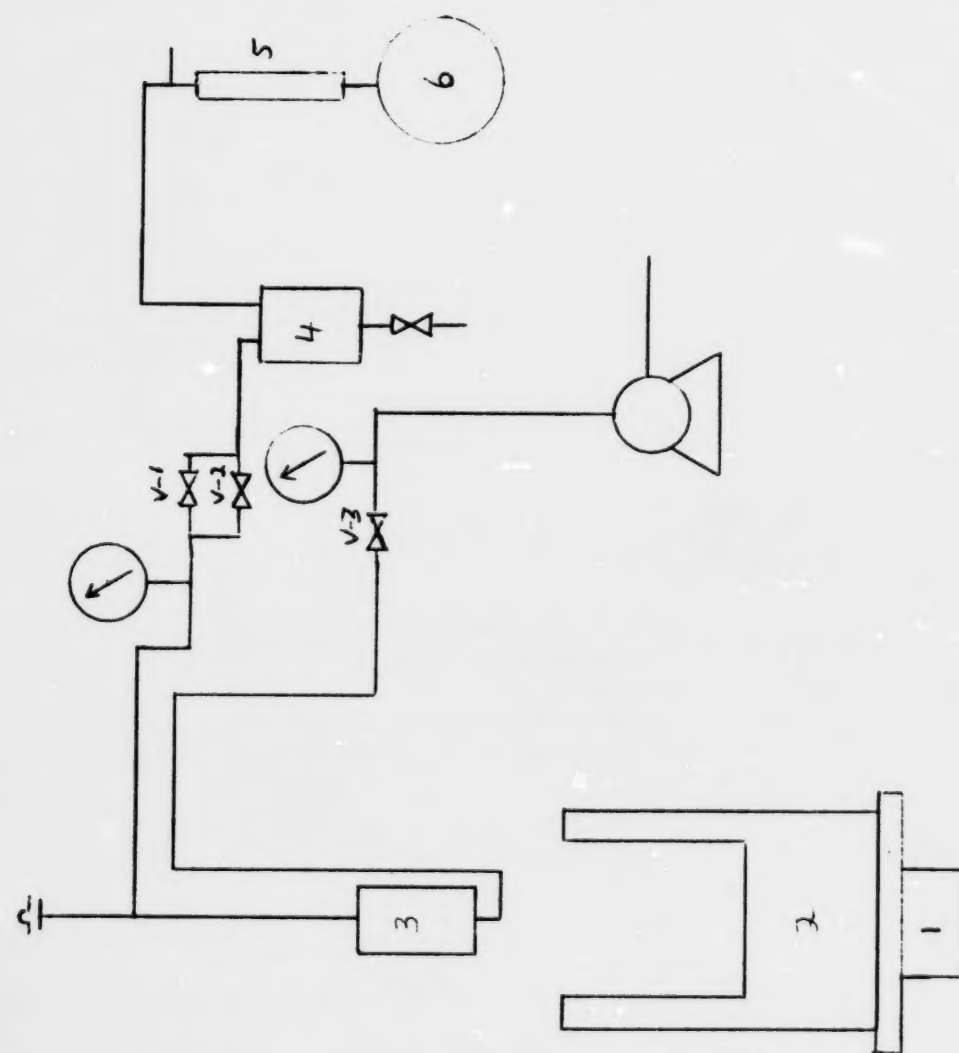
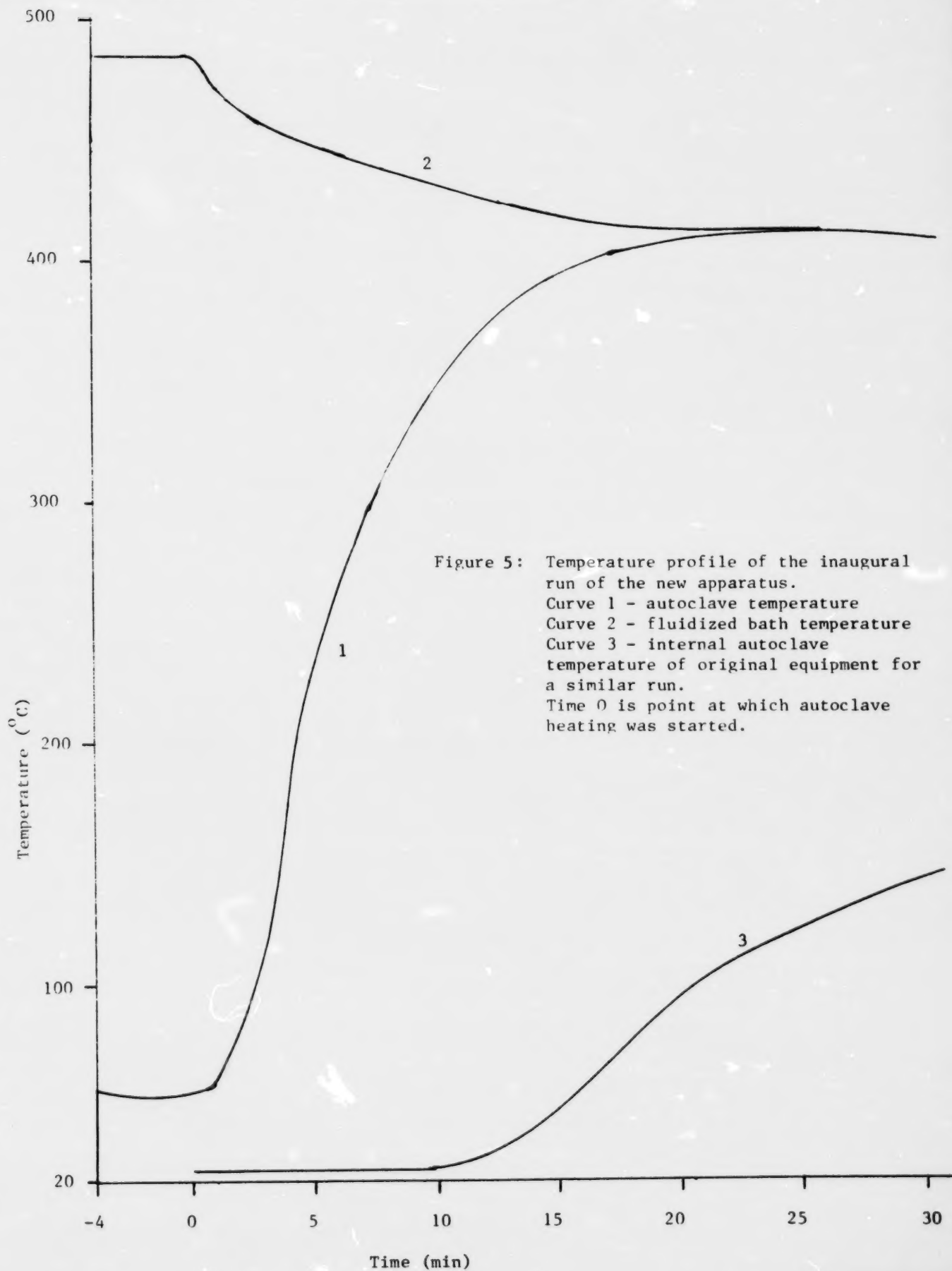


Figure 4: Schematic diagram of the assembled apparatus. 1 - jack; 2 - fluidized bath; 3 - reactor assembly; 4 - catch pot; 5 - condenser; 6 - recovered solvent receiver.



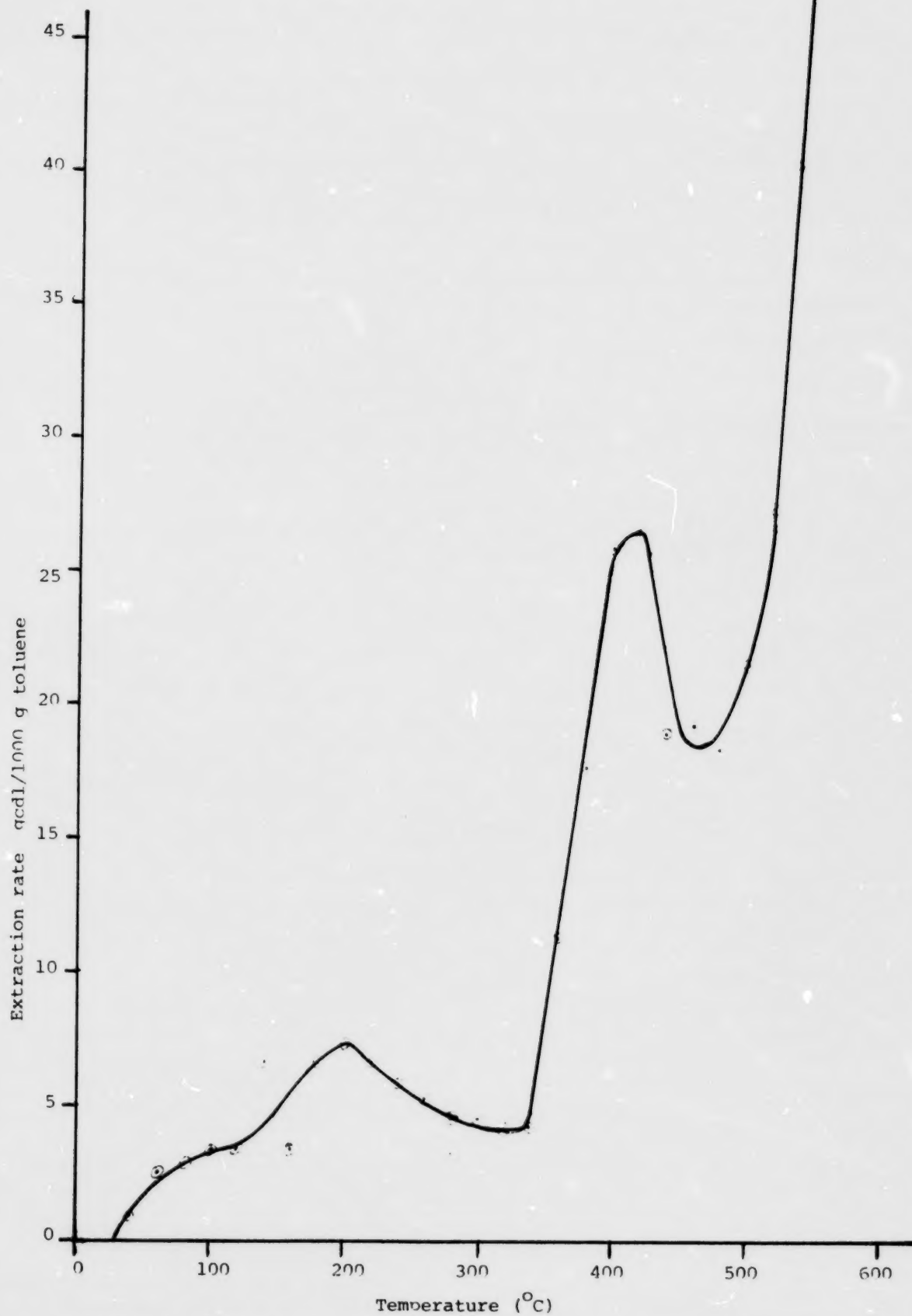


Figure 6: Plot of cdl extraction rate versus temperature for a toluene extraction of Forestburg subbituminous coal at 3000 psia.

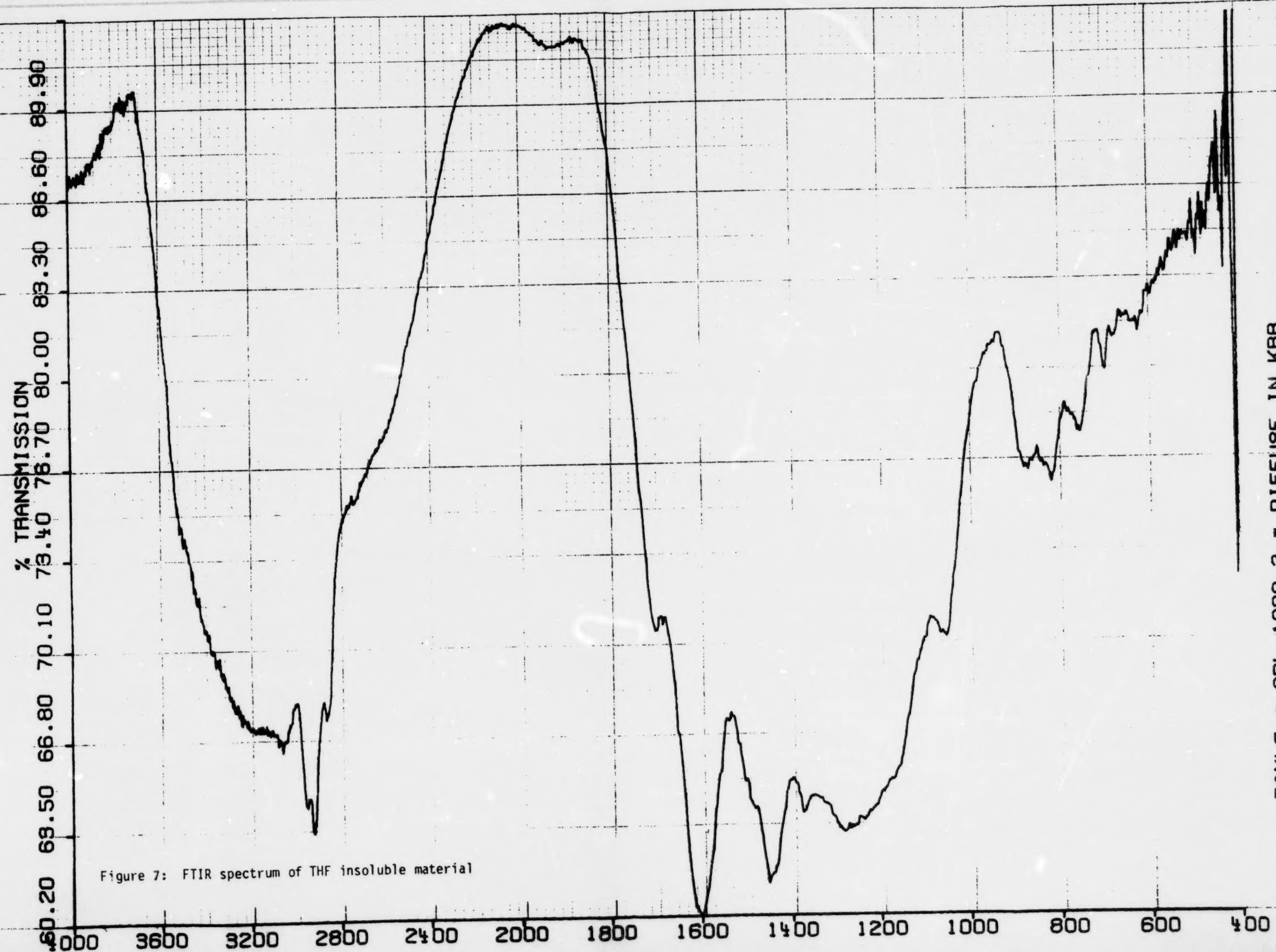


Figure 7: FTIR spectrum of THF insoluble material

RAYLO ■ CDL-1980-2 ■ DIFFUSE IN KBR
03/05/82 09:42:08

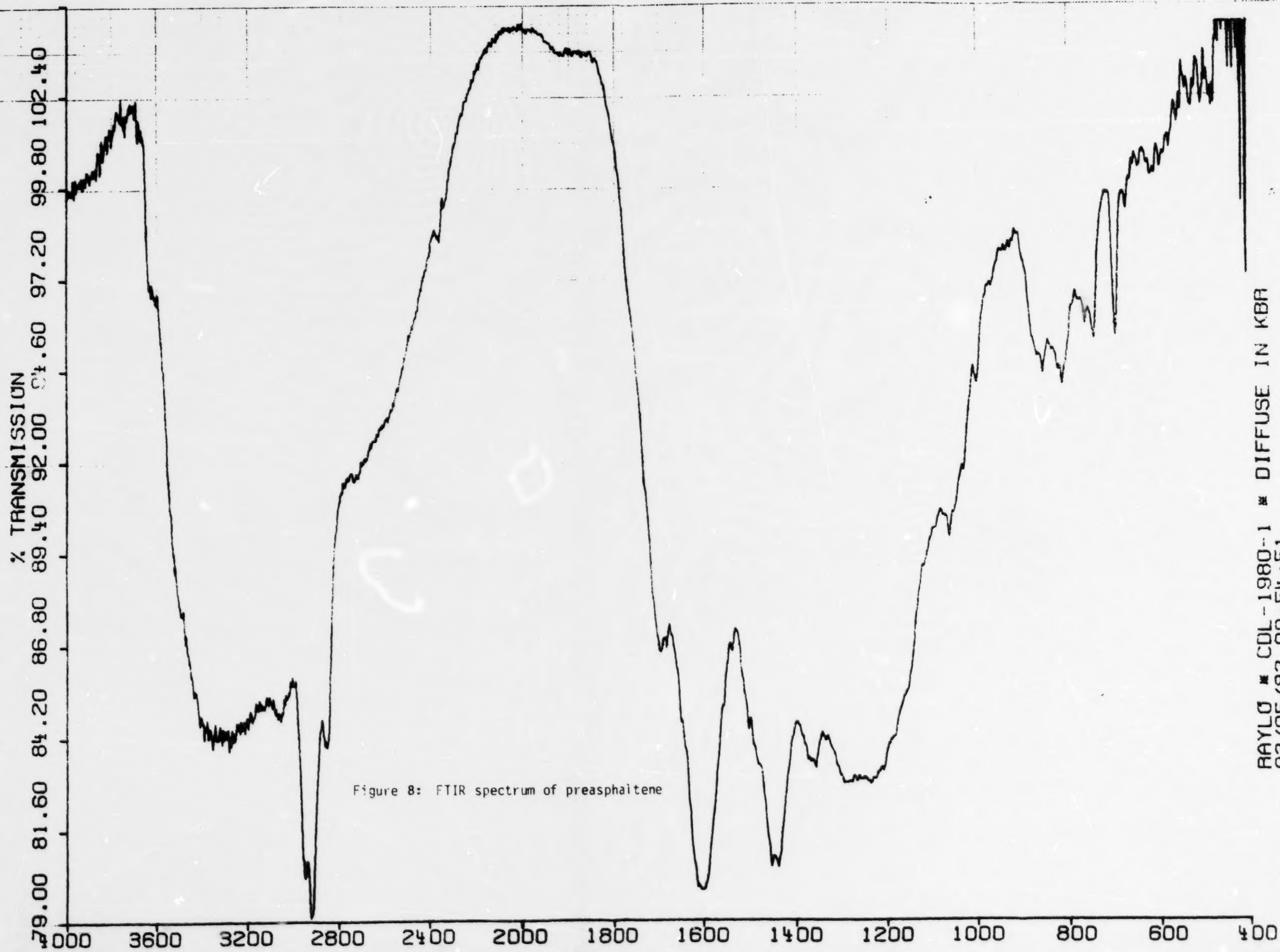


Figure 8: FTIR spectrum of preasphaltenes

RAYLO # CDL-1980-1 # DIFFUSE IN KBR
03/05/82 09:54:51

% TRANSMISSION

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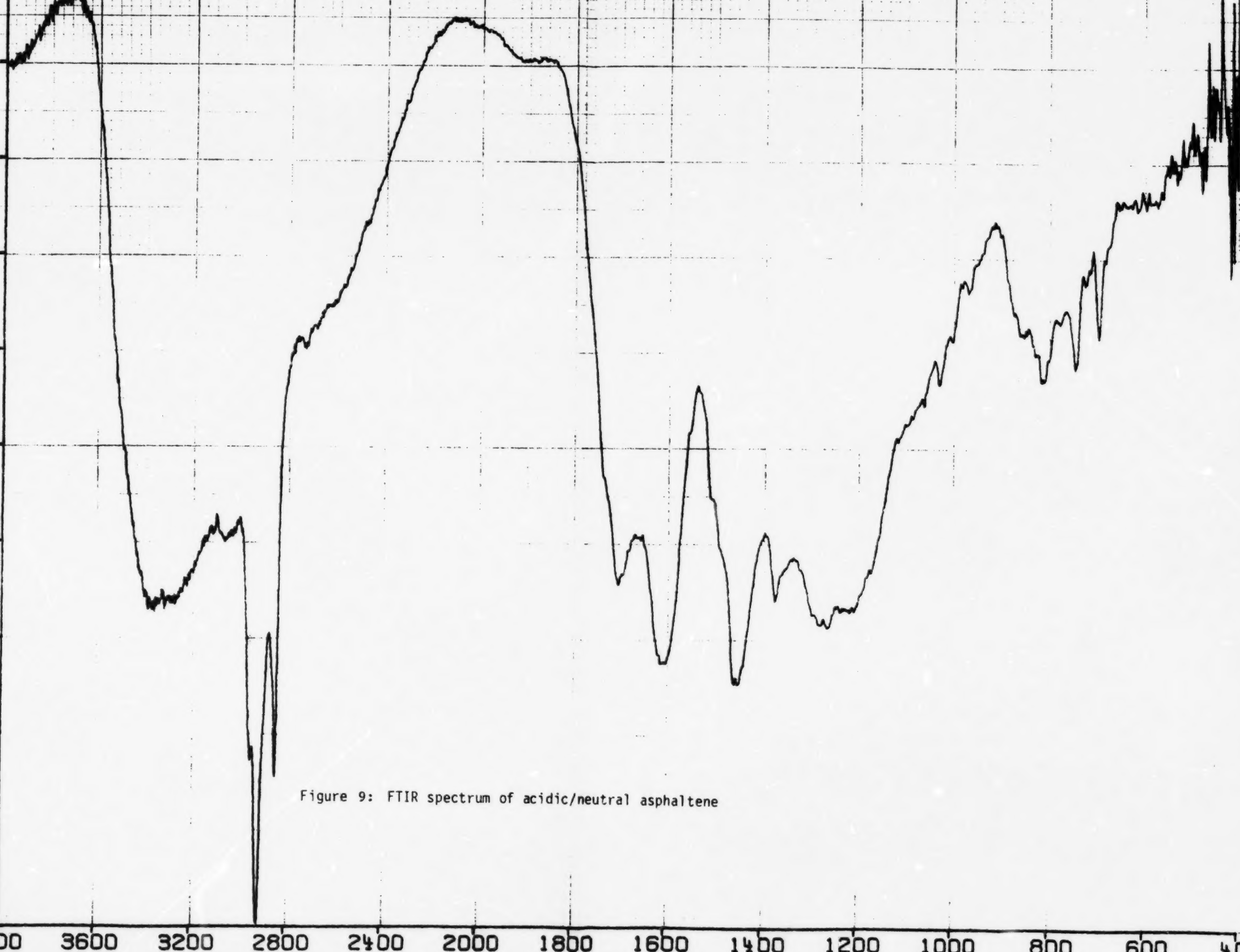


Figure 9: FTIR spectrum of acidic/neutral asphaltene

RAYLO ■ R187-7 H ■ DIFFUSE IN KBR
03/05/82 09:35:13

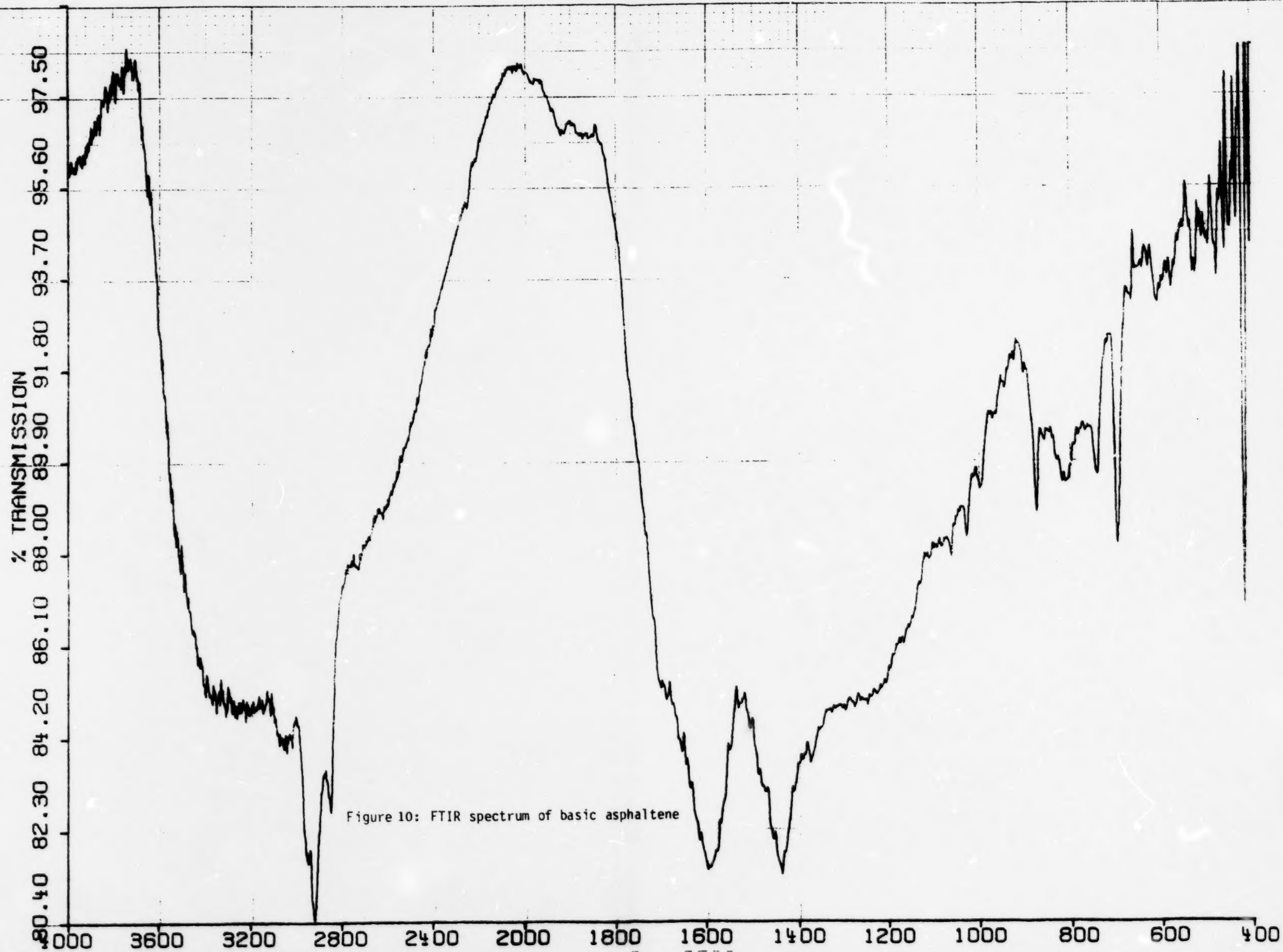


Figure 10: FTIR spectrum of basic asphaltene

RAYLO * R187-7 C * DIFFUSE IN KBR
03/05/82 09:30:43

RESEARCH MEMORANDUM

TO : R, Vukov, P. Van Bostelen

FROM: J.F. Prescott

DATE: June 22, 1981

RE : Visit to National Coal Board UK, Coal Research Establishment
Stoke Orchard, Cheltenham, UK on June 22, 1981

People seen: Dr. Derek F. Williams (Coal liquefaction methods)
Dr. John C. Whitehead (Chem Eng scg extraction)
Dr. Terry Martin (Head Analytical Section)
Dr. Allan Herod (mass-spectrometry)
Mr. Colin Snape (H^1 & C^{13} nmr - working at CRE
for external PhD at Leeds)

Dr. Thurston (Head of Department) was in Brussels.

Discussion

Our first meeting was with Williams and Whitehead. As agreed beforehand, A.G. released the final report of our first contract. There was not time during the meeting for them to read and talk but Derek Williams was very intent of finding out what we knew before they would say anything about their knowledge. Later on, after AG and I had been shunted round the analytical department, we found that they had absorbed the report and essentially agreed that what we had found was correct and more extensive than they expected. There are two variables (almost certainly but not expressed openly - solvent to coal ratio and residence time) which we have not studied. Their research had followed the course we have set. Their initial experiments were carried out in equipment very similar to ours. They then built a smaller unit (approx 40 g of coal) capable of being heated up in 2 - 3 min and they have carried out 2-3000 runs in this unit. They then progressed to a bench scale continuous unit (coal slurry feed, dynamic contactor, solid gas separator and liquid-gas separator) with a throughput of 0.5 kg/hr which they run for 8 hr putting through 2-3 kg of coal per run. We were not shown any of the laboratory equipment.

They admitted that their solvent was proprietary and would not discuss its composition and were reluctant to admit that its properties could be defined in general terms and assayed simply. They had reached the desirable solvent by the same means that we are using (the addition of co-solvents to toluene). When they realized that we knew the effect of hydrogen donor species they would not deny that this was important and would not discuss solvents further except to admit that they could be derived from the coal derived liquids after hydrotreating. They kept insisting that there were parameters which we have not investigated but were coy on the subject.

We visited the 5 kg/hr "bench scale" continuous unit which they would not call a pilot plant; it cost about £700,000 in 1977. They had fewer problems running it than expected. The famous picture shows only the feed mix-tank and the high pressure feed pump (Milton Roy). The actual reactor and separation units are in a concrete (12") bay behind the stuff shown in the picture. The purpose of the other vessels was not explained. The coal solvent slurry (coal:solvent ratio from 1:1 to 1:10) was recirculated round a loop by a centrifugal pump with a clear solvent seal flush obtained by passing a side stream from the pump outlet through a hydrocyclone and returning the thickened slurry to the pump inlet; this was done to avoid the addition of extra solvent to the system which would upset the mass balance. About 2% of the circulating slurry flow was pumped up to reaction pressure (not specified). They have not tried to minimize wear on the Milton Roy pump by flushing the packing but have changed the pump valve material to obtain a better life. The high pressure slurry, in a 1/4" OD heavy wall tube, is heated to reaction temperature (not specified) in a fluidized sand bath (external dimensions approx 36 x 36 x 36 which has explosion proof electrical heaters immersed in the bed). SC gas-solid contacting can be by entrained flow, in the same size tube (two coils presumably in series) in a second identical sand bath or in a fluidized bed contactor which is essentially an enlarged vertical tube (the fluidized solid is the coal itself). The fluidized bed is not necessary, the entrained flow is adequate. Solids are separated and are collected in a vertical tube which must be blown down and vacuum flashed at the end of the run. The char is pyrophoric if discharged above about 70°C. The method of gas solid separation was not disclosed; a cyclone would remove 95% of the solids but their method allows only a fraction of one percent of ash in the liquid product. The solid-gas separator is not typical of a commercial scale unit because of the fine grind of the coal (500 micron max) necessary for slurry flow in this scale. The isolation of the liquids is by pressure reduction, a temperature cycle was not effective, and the low solids content of the gas gives an acceptable life for the control valve. The product is then vacuum flashed and that from low rank coals will solidify at room temperature. Unfortunately, the liquid- and solid-gas separators were high up in the dark in the high bay and were virtually invisible. We did not see the control room which was separate. The unit was designed for 500°C and 6000 psi.

We were taken to see the liquid extraction unit which operates on about the same scale. Coal preparation and slurry make up is similar. The coal slurry is extracted with a heavier oil, a hydrogenated coal derived liquid fraction, at a temperature (unspecified) and at low pressure (10 bar). The extraction conditions are controlled carefully to give a reasonably low viscosity solution containing a readily filterable solid residue. The slurry is filtered on an approx. 18" dia single plate filter (two in parallel for alternate use) and the clarified unit which can be used for liquids obtained by either liquid or gas extraction.

The hydrotreating unit is standard and was, in fact, built by B.P.; they have aimed to produce liquids which do not require special treatment.

Possible commercialization

They envision a self contained plant in which the extraction is carried to a degree (about 40 - 45% liquid yield) at which the char would be consumed in generating the energy to run the plant and in gasification to produce the hydrogen required to convert the liquids to gasoline and diesel fuel. See the attached papers.

They insisted that the continuous unit results could only be assessed in reference to a specific plant configuration and that it would be necessary to work with them in this. Their initial response to a proposal for a continuous unit study was that they would have to carry out bench scale trials on the 40 g semi-continuous unit and on the 0.5 kg/hr continuous unit at a cost of about £5000 (for each coal) before they were prepared to run the 5 kg/hr continuous unit at about £10,000 per run (including analysis etc). After Williams and Whitehead had had some time to discuss the Raylo report, they modified their position on the laboratory bench work required. They said that with what we know and with what we are likely to know, if we continue on our research course, the laboratory bench work could be reduced to ensuring that the coal would not give trouble in the 5 kg/hr unit (e.g. caking).

Analysis

a) Coals and chars:

Little more than proximate and ultimate analysis is done. They would not comment on the use of specific tests (such as swelling) as indicators of coal suitability. The char is a poor to moderate active carbon and they have done petrographic analysis and pore size (mercury) determination.

b) Liquids:

(i) Mass Spectrometry

They attempt to vapourize the whole sample usually a deasphalted fraction of coal liquid in a bulb to obtain a characteristic sample but are limited to about 500 Daltons. They run the MS30 at 10 and 70 kV. Results are handled by a data processor and reported in tabular form; each row for a given carbon No. 6 to about 20 and each column the

the Z-number (-6 to -20). The Z-number is taken from the general hydrocarbon formula C_nH_{2n-Z} . The analyst was not sure what use the engineers made of the results. They also run gc-ms with a special type of capillary column which will give enough sample for the rather insensitive ms.

(ii) Nmr

They run a 60 MHz proton nmr (Perkin Elmer) and a C^{13} Brooker instrument. One of the attached papers shows how they manipulate the results for reporting in a useful form. They have a method of methylating (to about 80% conversion) coal liquids which both increases the solubility (allowing higher MW material to be analyzed) and gives more structural information. They measure the naphthenic to aromatic hydrogen ratio on samples of hydrogenated anthracene oil to assess their suitability as solvents for coal extraction. The content was scg extraction but liquid extraction might have been meant.

Conclusions

The research carried out at Raylo is vitally important. In general, the NCB will only reveal what we already know. Our research has been more effective than they expected and our research plans and the design of the next piece of equipment are such that we are likely to reach a good understanding of the system.

Finding a basis of agreement with the NCB CRE for the testing of Canadian coals on their 5 kg/hr continuous unit may not be easy. Their main objectives are to find potential customers for their process and equipment design and, more immediately, to strengthen their case for the construction of the 1 ton/hr pilot plant. Their overriding concern is to protect their proprietary knowledge of process conditions, including the nature of the extraction solvent, and the equipment design. Therefore, they will not disclose all the process conditions if they run a Canadian coal by their process. Optimization is, of course, only possible in the context of a proposed commercial design which defines, amongst other things, the product slate. Confidentiality agreements would be required.

In a later phone call to Derek Williams, I asked if they would run a Canadian coal in the 5 kg/hr unit using our solvent under conditions defined by us. He thought that this might be possible and that they would probably release all the process details but not the proprietary details of the equipment (eg solids separation method) in such a case. This approach would reveal our solvent and conditions and would not provide a comparison of our process with the NCB process. Clearly, CANMET must define their objectives very carefully before any agreement can be reached.

The NCB seemed quite disturbed about the intrusion of Raylo into the discussions. They were quite anxious to know what role Raylo would play and did not seem happy that I thought that Raylo would have a scientific and technical input particularly in the prior testing of Canadian coals. At one point, the NCB suggested that the results should be transmitted to CANMET through an independent engineering consultant who would "translate" the NCB results into a form acceptable to CANMET while keeping the information considered to be highly proprietary by the NCB confidential.

RESEARCH MEMORANDUM

TO : File

FROM: J.F. Prescott

DATE: June 26, 1981

RE : Supercritical Gas Extraction of Coal;
Inferences about the NCB process

Introduction

The information on which this report is based was mostly obtained during discussions with NCB held at Stoke Orchard Coal Research Establishment on June 19, 1981. Although some hard information was obtained many of the points are based on general knowledge of the system and inferences from what was said and not said. This description does not differ materially from the process described by John Whitehead at the Philadelphia AIChE Conference 1980.

Process Objective

The process is designed to be a self sufficient unit to make transport fuels, gasoline and diesel fuel (some LPG can be produced but can be recycled if not required as a product).

Process Outline

Coal would be air dried if necessary, ground to a mesh size of approximately 20 mesh, slurried in the liquid extraction solvent and the slurry pumped by piston pump up to the working pressure. The slurry passed through a 'preheater' which would in fact raise the temperature to the working value; the solvent would become supercritical some point in the preheater. The contact between the coal and the solvent could take place in entrained flow or in a fluid bed section, presumably depending on the desired residence time. The resulting gas-char slurry would pass to a solid-gas separator; virtually complete removal of solids is essential at this stage. The gaseous solution of the coal derived liquids in the supercritical solvent would then pass through a pressure let down valve to a liquid-gas separator. Both the char and the liquids would be subjected to vacuum stripping to recover the solvent.

Process Subunits

1. Coal drying:

This consists of air drying to remove the surface water to facilitate grinding. There was no suggesting that there would be any advantage in removing all the free water associated with the coal. There was no discussion of the role of - water in the extraction (ref Raylo experiment which showed that removal of all the free water before extraction gave lower yields in a semicontinuous run).

2. Coal grinding:

The preferred coal particle size was about 20 mesh. A much finer grind (less than 500 microns) had to be used in the 5 kg/hr continuous unit because of the smaller pipe sizes. They believed, as Raylo had found (Judith Potter's petrographic results) that penetration by the supercritical gases was complete for 20 mesh material.

3. Slurry preparation:

This would be done by continuous feed of the ground coal and solvent to a mixing tank. On the 5 kg/hr unit a batch of slurry is prepared for each run. The slurry is kept mixed both by an agitator (Lightnin twin propeller mixer) in the tank and by circulating the slurry past the high pressure pump heads by means of a centrifugal pump. They had incorporated a hydrocyclone across the circulating pump to produce a clear solvent stream to flush the mechanical seal on the pump.

4. Pumping to pressure:

The pump type for commercial operation was not discussed but it seems probable that it would be a piston pump. On the 5 kg/hr unit they used either one or both heads of a Milton Roy duplex pump. Pulsations were not as important a problem as had been expected. The material of construction of the pump valves had been changed to improve the life of the valves but they had not attempted to introduce a clear liquid flush to the packing; apparently mainly so as not to introduce a problem in estimating the solvent mass balance.

5. Preheating:

The slurry would be heated to the process temperature in a tubular furnace. On the 5 kg/hr unit this was an electrically heated fluidized sand bath. Full scale equipment would probably use gas fired furnaces but the proposed pilot plant was required to investigate the effects of convective and radiant heating.

6. Extraction contacting:

Two methods, entrained flow and fluidized bed, had been investigated. In either method, some extraction under entrained flow conditions takes place in the preheater. Both methods work. It is probable that the fluidized bed method (the coal being fluidized by the supercritical gas without an inert solid being present) was used to investigate prolonged residence times rather than the importance of back-mixing but this is a supposition.

7. Solids separation:

It was claimed that a more involved technique had to be used to separate the char from the supercritical gas solution on the 5 kg/hr unit than would be required on a production scale. This was said to be due to the finer grind of the coal on the small scale. As there seemed to be no intention to sieve out fines on the large scale and as attrition can be expected in the earlier steps it does not seem obvious that the production equipment would be simpler. A single stage cyclone would only remove 95% of the solids and was inadequate; other methods were not discussed.

8. Solids removal:

On the 5 kg/hr unit the solids were allowed to accumulate in a receiver and were treated and discharged as a separate job at the end of a run. Nothing was said about the method on a full scale plant but the inference was that it would be intermittent.

9. Solids treatment:

On the 5 kg/hr unit the solvent was flashed off from the char down to atmospheric pressure and then vacuum was applied. The associated condensers and receivers were not identified. The char can be pyrophoric especially if allowed to come into contact with air at temperatures above 70°C. The char has the surface area and pore structure of a moderately active adsorption carbon and can be activated to become a reasonably satisfactory ore. However, this is seen as only of minor interest. The chars are sufficiently active to be disposed of in a sludge pit.

10. Liquids separation and treatment:

Neither the method used on either the 5 kg/hr nor that proposed for use on a larger scale was discussed. The separation is induced by reducing the pressure although a temperature reduction method was mentioned in passing and was inferred to be inferior. It is not clear whether the pressure reduction also liquifies the solvent or not. Nor was it clear whether the coal derived liquids pass through a stage in which they are

dissolved in liquid extracting solvent. After pressure reduction, the residue is vacuum flashed to yield the liquid product which then will solidify on cooling, to room temperature (?). The condensers and receivers associated with these operations were not identified. It was not clear whether these steps were carried out continuously on the 5 kg/hr scale or whether the liquid product was allowed to accumulate at some stage after release of the pressure for the duration of a run.

11. Gaseous products:

Neither the composition nor the quantity of gaseous products released were revealed. The gaseous products were, however, not considered to be negligible and they seemed surprised that we did not consider them to be more important. Perhaps this indicates that they are operating at temperatures above our maximum of 450°C which is limited by our equipment.

12. Process conditions:

These were not discussed at all. The 5 kg/hr unit was designed to operate at 500°C and 6000 psi so as to be able to carry out experimental work at temperatures and pressures greater than those expected to be used commercially. The unit can operate with solvent to coal ratios from 1:1 to 10:1 and this ratio is considered to be a very critical variable in the economics of the process. It seems probable that they operate in the 2:1 to 4:1 range but this is pure supposition. Residence time can obviously be varied widely although not totally independently of the solvent to coal ratio. The rough calculation in Appendix A shows that residence times from 5 to 25 seconds can be achieved with the entrained flow contacting method.

13. Degree of extraction:

The NCB have achieved a maximum extraction of 70% of liquids from some coals. The economic degree of extraction is, however, much lower. At a yield of about 45% of liquids the process is balanced in that the amount of char produced is just sufficient to provide the hydrogen, by gasification, to hydrogenate the coal liquid to transport fuels and to provide sufficient energy to run the whole plant. The overall thermal efficiency was said to be above 65%.

APPENDIX A

Estimation of Residence Times

Assumption

1. Coal feed rate:

This was described as 4 - 5 kg/hr and the throughput per 8 hr run as about 25 to 35 kg suggests that the 5 kg/hr value is a maximum which is probably only achieved at low solvent to coal ratios.

2. Tubing size:

The tubing visible in the second fluidized sand bath seemed to be 1/4" OD but was described as 3 - 4 mm ID. 1/4" x 0.049" or 1/4" x 0.069" tubing would fit the description, the lighter wall tube having an ID of 3.86 mm and the heavier wall tube having an ID of 3.05 mm. The allowable working pressures for 304 SS at up to 100°F are 8,700 and 11,718 psi respectively (Swagelok Handbook). From Table UHA-23 (ASME Unfired Pressure Vessels) changing to 316 SS at 900°F (ca 500°C) the working pressures would be reduced to 7400 and 9900 psi. Either tube would be usable but my preference would be for the 1/4 x 0.069 wall tube which has an internal cross-sectional area of 0.073 cm².

3. Entrained flow (expecially for low residence time)

If the extraction taking place in the preheater is ignored and the extraction reactor (twin coil) is assumed to be 40 ft in length (2 x 20 ft standard tube lengths in series because parallel flow would be impossible to achieve on this scale), then the residence time can be calculated on the following assumptions:

- a) Coal feed rate 5 kg/hr.
- b) Solvent to coal ratio 1:1 by weight.
- c) Solvent density 0.90 g/ml as liquid.
- d) Solvent density 0.40 g/ml as supercritical gas.
- e) Coal density 2.40 g/ml under both conditions.

then

- a) Average vol (subcritical) = 1.53 ml/g of coal feed.
- b) Average vol (supercritical) = 2.92 ml/g of coal feed.

and for 5 lb/hr coal feed rate

- c) Volumetric flow (subcritical) = 7.65 l/hr.
- d) Volumetric flow (supercritical) = 14.6 l/hr.

../2

and for 1/4 x 0.065" wall tubing

- e) Linear flow rate (subcritical) = 0.96 ft/sec.
- f) Linear flow rate (supercritical) = 1.83 ft/sec,

these values are well below the limiting velocity

so for 40 ft of tubing

- a) the residence time (supercritical) is 22 seconds which seems a reasonable value.

If the solvent to coal ratio was increased to 5:1 by weight, the linear velocity (supercritical) would be raised to about 8.07 ft/sec (still acceptable) and the residence time reduced to about 5 sec.

APPENDIX III

Petrographic analysis of chars derived from toluene and tetralin-toluene extractions of Forestburg subbituminous coal at 400°C and 1900 psig.

23SQ-23440-0-9111-S-2	Forestburg coal
-SCL-0	100% toluene
-SCL-2	2% tetralin in toluene
-SCL-5	5% tetralin in toluene
-SCL-10	10% tetralin in toluene
-SCL-15	15% tetralin in toluene

Petrographic analysis of residues from toluene/tetralin
extraction of sub-bituminous coal
(Raylo Chemicals Ltd.)

General:

The effects of supercritical tetralin/solvent extraction of sub-bituminous coal — S-2 were assessed petrographically following examination of the benzene insoluble residues SCL-0, SCL-2, SCL-5, SCL-10 and SCL-15. These effects are summarized by considering:

a) The relative amounts of isotropic : anisotropic carbon in the residue; the formation of anisotropic carbon is considered to be detrimental to liquid yields.

b) The degree of vesiculation (ie. the presence of voids or vesicles in the residues); this is considered to indicate the amount of volatile material lost or extracted from the coal.

c) The changes in the nature of the coal macerals; this gives some idea of how they respond to the supercritical gas and demonstrates the effect of coal composition on conversion.

d) The presence of materials that are not coal residues but may be products of the extraction process that are redeposited on the coal particles or trapped within them.

Description of the coal feedstock, 2380-23440-0-9111-S-2

The coal was a relatively low ranking, sub-bituminous coal ($R_o = 0.36$), vitrinite rich and very low in other macerals giving a reactivities:inerts ratio of 25. Over half of the vitrinite was highly structured telinite and telocollinite. Petrographic analysis is given in Table 1.

TABLE 1
Petrographic composition of 2380-23440-0-9111-S.2

1. Maceral Group

		Structured	51.6
Vitrinite	92.4	Groundmass	28.4
		Unstructured	12.4
Inertinite	3.6		
Liptinite	3.2		
Mineral	-		
	100		

2. Reactives: Inerts Ratio : 24.6

3. Reflectance, $R_{AV} = 0.36$

Description of residues from supercritical gas extraction of coal

-SCL-01 SCL-2, SCL-5, SCL-10 and SCL-15

The five residues were petrographically similar in the composition, morphology and reflectance of the vitrinite-derived components. They were isotropic chars in which the vitrinite and inertinite-derived components were recognizeable, but not liptinites. The vitrinite residues showed increases in reflectance (R_0) of between 0.82-0.6% over that of the feedstock (0.36%); this probably indicates a relative increase in the carbon content of approximately 12-15%. The vitrinite residue also showed signs of vesiculation i.e. the development of vesicles or gas release holes,

The extent of vesiculation was described as vesicular, perforated or non-vesicular depending upon the density and size of the vesicles*. The results of the analyses are given in Table 2. The following features were commonly observed in all of the residues:

1) Vesiculation was not extensively developed in any of the residues; when it was observed it was mostly found in structured vitrinite char.

2) Most of the particles had a 'perforated' appearance and this was commonly related to the morphological structure of the vitrinites.

The total amount of perforated and vesicular char was greater in residues -SCL-5 and SCL-15.

3) A large portion of the vitrinites did not exhibit perforation or vesiculation.

4) Inertinite Macerals appeared unchanged.

5) Liptinite macerals were not present in their original state; some of the perforations observed in groundmass vitrinite may have been produced by reaction of the hydrogen-rich liptinites but these comprised only 3.2% of the coal.

* See definition of textures.

6) Some weakly-fluorescing, dark brown, resin-like material (or oil-like) was observed infilling voids in Inertinite and Structured huminite chars. (Miscellaneous in Table 2).

7) No anisotropic carbon was observed.

8) No redeposition of any of the extracted materials appeared to have taken place.

Discussion and Interpretation of the results

While the residues do not appear to be as highly altered as those produced by other coal liquefaction processes, some changes occurred that can be interpreted in terms of the reaction of the coal to extraction by toluene/other hydrogen donor solvents.

Firstly, the residues are completely isotropic. This is significant since the residue -SCL examined under the previous contract contained 24% anisotropic semicoke. Semicoke formation is the principal cause of reactor fouling and results in reduced liquid yields.

Secondly, the residues were pitted with small holes and were referred to as perforated or vesicular. True vesiculation was poorly developed in all five residues and confined to the structured vitrinite char; most of the groundmass vitrinite was perforated by small vesicles but some of this may have resulted from destruction of the contained liptinite macerals. If the vesiculation could be related to the amounts of gases/liquid extracted from this coal and therefore to the penetration of the supercritical gases, then this would suggest that yields were not as great as with other solvents (OSU80-00088) and penetration by the gases was neither as effective nor as evenly distributed around the reactor as in previous observations of coal residues extracted with toluene/tetralin. The penetrating power of tetralin/other hydrogen donors appeared to be approximately the same except possibly a little better in experiments SCL-5 and SCL-15.

In residues SCL-0, SCL-5 and SCL-15, there was weakly-fluorescing material trapped in voids in inertinite and structured vitrinite chars (Plate) which appeared to be either hydrogen-rich material produced from the coal or mineral matter trapped in voids. Minor amounts of similar material were observed in the feedstock but it was more like the maceral resinite and was not as common. No carbonaceous deposited were developed.

Petrographic Analysis %	RESIDUE				
	SCL-0	SCL-2	SCL-5	SCL-10	SCL-15
<u>VESICULAR</u>					
structured vitrinite	4.0	3.6	5.4	4.4	5.0
groundmass vitrinite	0.6	0.6	0.9	1.0	1.0
<u>PERFORATED</u>					
structured vitrinite	9.3	13.8	19.0	16.8	14.9
groundmass vitrinite	27.1	27.1	23.0	22.6	27.0
<u>NON-VESICULAR</u>					
structured vitrinite	55.4	55.4	48.3	51.4	47.2
groundmass vitrinite	-	-	-	-	-
INERTINITE	2.6	4.2	2.7	3.2	2.7
MINERAL	0.8	0.8	0.2	0.6	1.0
MISCELLANEOUS	0.2	-	0.5	-	1.2
<u>REFLECTANCE</u>					
R _o AV	1.03	1.13	1.11	1.08	1.18

TABLE 2

Petrographic analysis of residues from supercritical
gas extraction of sub-bituminous coal (-S.2) by
toluene/other hydrogen donor solvent mixtures

TEXTURES

Non-vesicular: vitrinite appears morphologically unchanged except for an increase in the reflectance (which reflects an increase in the carbon content).

Vesicular: the vitrinite residue exhibits lots of large rounded vesicles that may be attributed to evolution of gas and liquids and also shows an increase in reflection. This is most commonly developed in the structured vitrinite residue.

Perforated: the vitrinite is pitted with tiny vesicles rather than large gas release holes. These perforations may have developed as (a) a result of liptinite macerals reacting and/or (b) as a result of minor amount of gas or liquid loss.

Petrographic Composition of 23SQ.23440-0-9111-S-2

Maceral Group	%	Maceral	%
VITRINITE	: 92.4	Structured	: 51.6
		Groundmass	: 28.4
		Unstructured	: 12.4
		Telocollinite	: 51.6
INERTINITE	: 3.6	Desmocollinite	: 28.4
		Corpocollinite	: 10.4
		Gelocollinite	: 2.0
		Fusinite	: 1.2
LIPTINITE	: 3.2	Semifusinite	: 1.6
		Inertodetrinite	: 0.8
		Sporinite	: 2.0
		Resinite	: 0.8
MINERAL MATTER		Liptodetrinite	: 0.4
REACTIVES: Inerts Ratio: 24.64			
Reflectance: $R_o AV$ = 0.361			
Std. Dev.= 0.05			
Variance = 0.002			

TABLE 1

Results of petrographic analysis of the coal feedstock

Petrographic Composition of 23SQ.23440-0-9111-SCL-0

Texture	Origin of residue	%
No Devolatilization : 55.4	Structured	
	vitrinite :	68.7
Perforated : 9.3		
Vesicular : 4.0		
No Devolatilization : 0.0	Groundmass	
	vitrinite :	27.7
Perforated : 27.1		
Vesicular : 0.6		
	Inerts :	2.6
	Mineral	
	Matter :	0.8
	Miscellaneous:	0.2
		<u>100</u> %

NOTE: 41.0 of the residue showed signs of gas/
liquid release. 36.4% was perforated and
4.6 was vesicular.

Reflectance: R_{AV} = 1.03
Std. Dev. = 0.15
Variance = 0.02

Petrographic Composition of 23SQ.23440-0-9111-SCL-2

Texture	%	Origin of residue %
No Devolatilization :	55.4	Structured vitrinite : 72.8
Perforated :	13.8	
Vesicular :	3.6	
No Devolatilization :	0.0	Groundmass vitrinite : 22.2
Perforated :	21.4	
Vesicular :	0.8	
		Inerts : 4.2
		Mineral Matter : 0.8
		Miscellaneous: 0.0
		100 %

NOTE: 39.6% of the residue showed evidence of gas/liquid release. 35.2% was perforated and 4.4% was vesicular.

Reflectance: R_{AV} = 1.13
 Std. Dev. = 0.16
 Variance = 0.03

Petrographic Composition of 23SQ.23400-0-9111-SCL-5

Texture	%	Origin of residue %
No Devolatilization :	48.3	Structured vitrinite : 72.7
Perforated :	19.0	
Vesicular :	5.4	
No Devolatilization :	0.0	Groundmass vitrinite : 23.9
Perforated :	23.0	
Vesicular :	0.9	
		Inerts : 2.7
		Mineral Matter : 0.2
		Miscellaneous: 0.5
		<u>100</u> %

NOTE: 48.3% of the residue was vesicular or perforated.
42.0% was perforated and 6.3% was vesicular.

Reflectance: R_{0AV} = 1.11%
Std. Dev. = 0.16
Variance = 0.03

Petrographic Composition of 23SQ.23440-0-9111-SCL-10

Texture	%	Origin of residue %
No Devolatilization :	51.4	Structured vitrinite: 72.6
Perforated :	16.8	
Vesicular :	4.4	
No Devolatilization :	0.0	Groundmass vitrinite : 23.6
Perforated :	22.6	
Vesicular :	1.0	
		Inerts : 3.2
		Mineral Matter : 0.6
		Miscellaneous: 0.0
		<u>100 %</u>

NOTE: 44.8% of the residues showed signs of gas/ release. 39.4% was perforated, 5.4% was vesicular.

Reflectance : R_{0AV} = 1.08
 Std. Dev. = 0.15
 Variance = 0.02

Petrographic Composition of 23SQ.23440-0-9111-SCL-15

Texture	%	Origin of residue	%
No Devolatilization :	47.2	Structured vitrinite :	67.1
Perforated :	14.9		
Vesicular :	5.0		
No Devolatilization :	0.0	Groundmass vitrinite :	28.0
Perforated :	27.0		
Vesicular :	1.0		
		Inerts :	2.7
		Mineral Matter :	1.0
		Miscellaneous:	1.2
			100

NOTE: 47.9% of the residue was perforated or vesicular.
41.9% was perforated and 6.0% was vesicular.

Reflectance : R_{AV} = 1.18 %
Std. Dev. = 0.17
Variance = 0.03

**POOR
QUALITY
ORIGINAL**